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CHLOROTRIFLUOROETHYLENE DECAY
IN THE ATMOSPHERE: CONTROLLED-
ENVIRONMENT CHAMBER STUDIES

DANIEL A. STONE AND JAMES R. LONG

HEADQUARTERS AIR FORCE CIVIL
ENGINEERING SUPPORT AGENCY
RAVC

TYNDALL AFB, FL 32403-6001

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This report documents a series of experiments conducted to shed additional light on the role of surface-catalyzed reactions on the potential atmospheric oxidation of CTFE vapor. The experiments were conducted in a controlled-environment chamber consisting of a one-meter diameter stainless steel sphere which is Teflon® coated. Vapor-phase CTFE was introduced into the chamber at the 5-10 ppm concentration level. It was exposed to helium, then helium with 20 percent oxygen, then helium with 20-50 ppm ozone added, and to humid (~75 percent R.H.) helium, both with and without oxygen. After these initial experiments were concluded, 20 corroded aluminum plates were added to the chamber which increased its surface area by about a factor of ten. Then CTFE was introduced with dry helium, helium plus oxygen, and helium plus ozone.					
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The results showed that CTFE was strongly adsorbed to the surfaces in the chamber, both Teflon® and the added plates. However, there was no evidence for the occurrence of any chemical reactions, even with ozone present.

Literature studies suggest that CTFE may be photodegraded on surfaces by the action of sunlight in a surface-catalyzed process. This aspect of the potential environmental fate of CTFE should be pursued by additional research.

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EXECUTIVE SUMMARY

A. OBJECTIVE: This research was conducted to extend our knowledge of the chemical and physical processes which control the eventual fate of vapor-phase chlorotrifluoroethylene (CTFE) in the environment. The studies were conducted in a controlled-environment chamber designed to simulate various conditions which would be representative of those which CTFE vapors would encounter in operational settings.

B. BACKGROUND: Hydraulic fluids are an important constituent of many modern military weapons systems. The petroleum-based fluids first used in hydraulic systems were responsible for a significant number of aircraft fires because of their flammability. Since the early seventies, researchers at several U.S. military installations have sought to develop a new class of hydraulic fluids which would have increased performance capabilities and be nonflammable. Several interim, fire-resistant, fluids were developed, but the ultimate goal remained an entirely nonflammable hydraulic fluid.

Researchers at the Air Force Materials Laboratory at Wright-Patterson AFB began a program in 1975 to develop a new hydraulic fluid with the required properties. Of the many potential candidates, chlorotrifluoroethylene (CTFE) was eventually selected because it is nonflammable and has the required physical properties. The initial positive evaluation of CTFE as a replacement hydraulic fluid has been tempered by subsequent toxicological studies of this material. Exposure studies at the Toxic Hazards Division, Harry G. Armstrong Aerospace Medical Research Laboratory, Wright-Patterson AFB, led to the conclusion that CTFE vapors could have measurable toxic effects under some circumstances. This finding provided the impetus for RAVC studies to determine the expected atmospheric lifetime of CTFE vapors in an attempt to provide additional data for an overall risk assessment of this material.

C. SCOPE: The study began with a determination of the stability of CTFE vapors under inert conditions to establish its inherent interactions with the controlled-environment chamber. Then the effects of adding oxygen, moisture, and ozone were determined. The effects of adding additional reactive surfaces to the chamber were also evaluated. Eventual goals were to modify the chamber to include a powerful light source which would enable the evaluation of surface-enhanced photochemical degradation studies. However, the reassignment of the principal investigator and his assistant led to a conclusion of the research before photochemical studies could be undertaken. This report summarizes the research which was completed.

D. **METHODOLOGY**: The research was conducted in the Environics Laboratory controlled-environment chamber. CTFE was obtained from Wright-Patterson AFB. Species concentrations in the chamber were monitored principally by Fourier transform infrared (FT-IR) spectroscopy; some measurements were also taken with a residual gas analyzer.

E. **TEST DESCRIPTION**: The study was done in progressive steps. First the stability/reactivity of CTFE in the empty chamber in an inert atmosphere was determined. Then the effects of adding oxygen, moisture, and ozone were measured. Finally, 20 corroded aluminum plates were added to the chamber increasing the interior surface area by about a factor of 10. CTFE stability/reactivity was then reevaluated with these plates present.

F. **RESULTS**: Because it is a fully halogenated species, CTFE is not expected to undergo reactions in the open troposphere and its reactivity on surfaces was expected to be low. The results of the studies completed to date bear out these expectations. CTFE did not react in the presence of oxygen or ozone in the presence or absence of added surfaces according to the results of this study.

G. **CONCLUSIONS**: CTFE appears to be strongly adsorbed onto the surfaces it contacts. It is partially desorbed by water vapor. It does not appear to react on surfaces or in the atmosphere in the absence of sunlight. The strong sorption tendency and the likelihood of slow desorption lead to some concern about operational settings where small spills over a long period of time could produce enough vapor-phase CTFE to cause exposure problems.

H. **RECOMMENDATIONS**: Studies from the literature suggest that CTFE would likely undergo photoassisted degradation reactions on the soil and perhaps other surfaces. Because of this likelihood, eventual project goals were to modify the chamber to include a powerful light source which would enable the evaluation of surface-enhanced photochemical degradation studies. However, the reassignment of the principal investigator and his assistant led to a conclusion of the research before photochemical studies could be undertaken. If possible, the chamber modifications should be completed and the photodecomposition experiments undertaken.

PREFACE

This report was prepared by the Civil Engineering Laboratory of the Air Force Civil Engineering Support Agency (AFCESA), Tyndall Air Force Base FL 32403-6001.

This research was sponsored by AFCESA. Dr Daniel A. Stone and Mr James R. Long (AFCESA/RAVC) were the government project officers. This report summarizes work accomplished between October 1990 and November 1991 under program element 61101F.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.



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SECTION I

INTRODUCTION

A. OBJECTIVE

This research was conducted to extend our knowledge of the chemical and physical processes which control the eventual fate of vapor-phase chlorotrifluoroethylene (CTFE) in the environment. The studies were conducted in a controlled-environment chamber designed to simulate various conditions which would be representative of those which CTFE vapors would encounter in operational settings.

CTFE spills can occur during both normal operations and in accidents. The vapors which escape have a finite lifetime, which depends on their interactions with surfaces and in the open atmosphere. Since CTFE is a fully halogenated species, it is expected to be unreactive with respect to gas-phase tropospheric processes. However, its interactions with surfaces have not been characterized and were the principal goal of this effort.

B. BACKGROUND

Hydraulic fluids are an important constituent of modern military weapons systems. The petroleum-based fluids first used in hydraulic systems were responsible for a significant number of aircraft fires because of the flammability of these fluids. Since the early seventies, researchers at U.S. military installations have sought to develop a new class of hydraulic fluids which would have increased performance capabilities and be nonflammable. Several interim, fire-resistant, fluids were developed, but the ultimate goal remained an entirely nonflammable hydraulic fluid (Reference 1).

Researchers at the Air Force Materials Laboratory at Wright-Patterson AFB began a program in 1975 to develop a new hydraulic fluid with the required properties. Of the many potential candidates, four classes of fluids were able to meet the initial performance requirements: chlorofluorocarbons, fluoroalkylethers, linear perfluoroalkylethers, and perfluoroalkylether triazines. Of these, CTFE was eventually selected (Reference 2). The choice has also been analyzed and documented by Mahony (Reference 3). A brief developmental history and summary of properties are provided by a commercial vendor (Reference 4).

The initial positive evaluation of CTFE as a replacement hydraulic fluid has been flagged by subsequent toxicological studies of this material. Exposure studies at the Toxic Hazards Division, Harry G. Armstrong Aerospace Medical Research Laboratory, Wright-Patterson AFB, (References 5-8) led to the conclusion that CTFE vapors could have measurable toxic effects under some circumstances. This finding provided the impetus for RAVC studies to determine the expected atmospheric lifetime of CTFE vapors in an attempt to provide additional data for an overall risk assessment of this material.

C. SCOPE

The study began with a determination of the stability of CTFE vapors under inert conditions to establish its inherent interactions with the controlled-environment chamber (References 9 and 10). Then the effects of adding oxygen, moisture, and ozone were determined. The effects of adding additional reactive surfaces to the chamber were also evaluated. Eventual goals were to modify the chamber to include a powerful light source which would enable the evaluation of surface-enhanced photochemical degradation studies (References 11 and 12). However, the reassignment of the principal investigator led to a conclusion of the research before photochemical studies could be undertaken. This report summarizes the research which was completed.

SECTION II

EXPERIMENTAL PROCEDURES

A. SPHERICAL REACTION CHAMBER

To ensure maximum control over experimental variables in this study, a spherical, stainless steel reaction chamber was employed. The design and construction details for this chamber have been previously described (References 9 and 10) and will only be briefly outlined here.

The primary design consideration for this chamber was to minimize surface interactions. To this end, a spherical design was adopted giving the lowest surface-to-volume ratio of any simple geometrical solid. The chamber was also coated with a 10-mil thick layer of FEP Teflon®. The size of the chamber was chosen to give a reasonable tradeoff between optical path length and internal volume. The choice of a 1-meter diameter sphere gave a working optical path length of 106 meters while maintaining a manageable volume of about 525 liters.

The chamber was constructed of 3/16-in stainless steel hemispheres welded together. Three 12-inch circular ports are welded to corresponding openings in the chamber wall. Two are diametrically opposed across the horizontal diameter. These contain mounts for the long-path infrared optics. The third port is placed at right angles to the line joining the other two. It is used for introducing surface samples into the chamber. There are several other ports in the chamber wall. One 4-inch optical view port is placed above each of the 12-inch mirror mounting ports, which facilitates mirror alignment. There are additional ports for pressure measuring devices, a temperature/humidity probe, a stirring fan, and a high-vacuum pumping station.

The chamber has copper coils welded to its outer surface for temperature control. It is also surrounded by 1.5 inches of Rubatex® high-density foam insulation. With the heating/cooling recirculation unit operating, the chamber temperature can be varied from 6.4 °C to 46.6 °C. Normal operating temperature is 20 °C.

A control panel and glass sample introduction manifold are mounted on an aluminum frame which is attached to the chamber on the side opposite the sample introduction port. The control panel provides a mount for the temperature gauge and for two different pressure gauges.

The optical system for the chamber was designed to provide the maximum possible pathlength within the 1-meter mirror separation constraint. This was accomplished by using a modification of the basic White (Reference 13) three-mirror system as suggested by Olson (Reference 14). The chamber optical system is interfaced to a Nicolet Model 160-SX Fourier transform infrared (FT-IR) spectrometer. The optical interface diagram and other details of the optical system have been provided in earlier work (References 9 and 10).

An additional capability was added to the chamber for this research effort, a residual gas analyzer (RGA) with an atmospheric pressure sampling accessory. The unit is a Hiden Analytical HAL 2/200 RGA with atmospheric sampling capability. It was attached to the spherical chamber via a new extension flange assembly which was fabricated by Nor-Cal Products (Yreka, CA). Two connections were made between the chamber flange and the RGA: a high-vacuum connection through a 2-inch diameter by 36-inch long flexible stainless steel tube with a 2 3/4-inch, copper gasket, high-vacuum flanges on each end, and an atmospheric pressure sampling connection through a 2-foot section of 1/16-inch stainless steel tubing. The chamber with the RGA present are shown schematically in Figure 1.

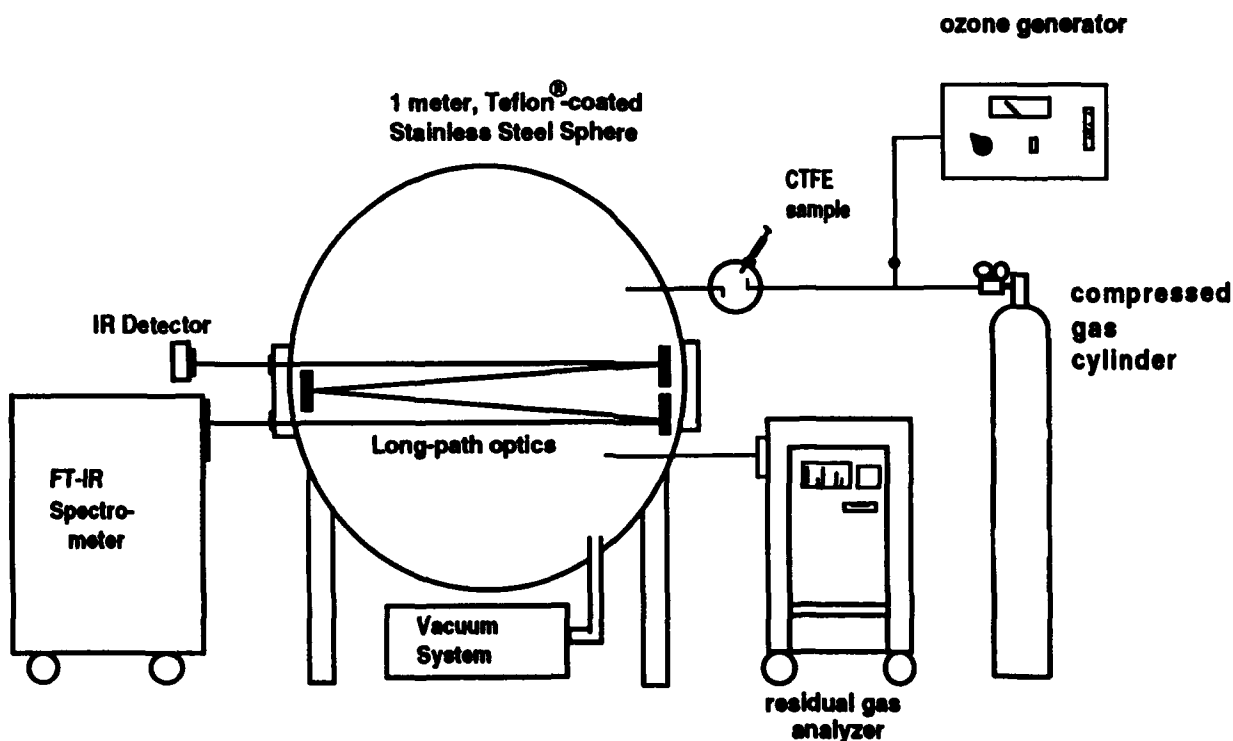


Figure 1. Schematic Diagram of Experimental Apparatus

The new extension flange assembly was bolted onto the sample port of the original chamber (see References 9 and 10 for more detailed drawings of the chamber) sample port. The features of the new extension are shown in Figure 2.

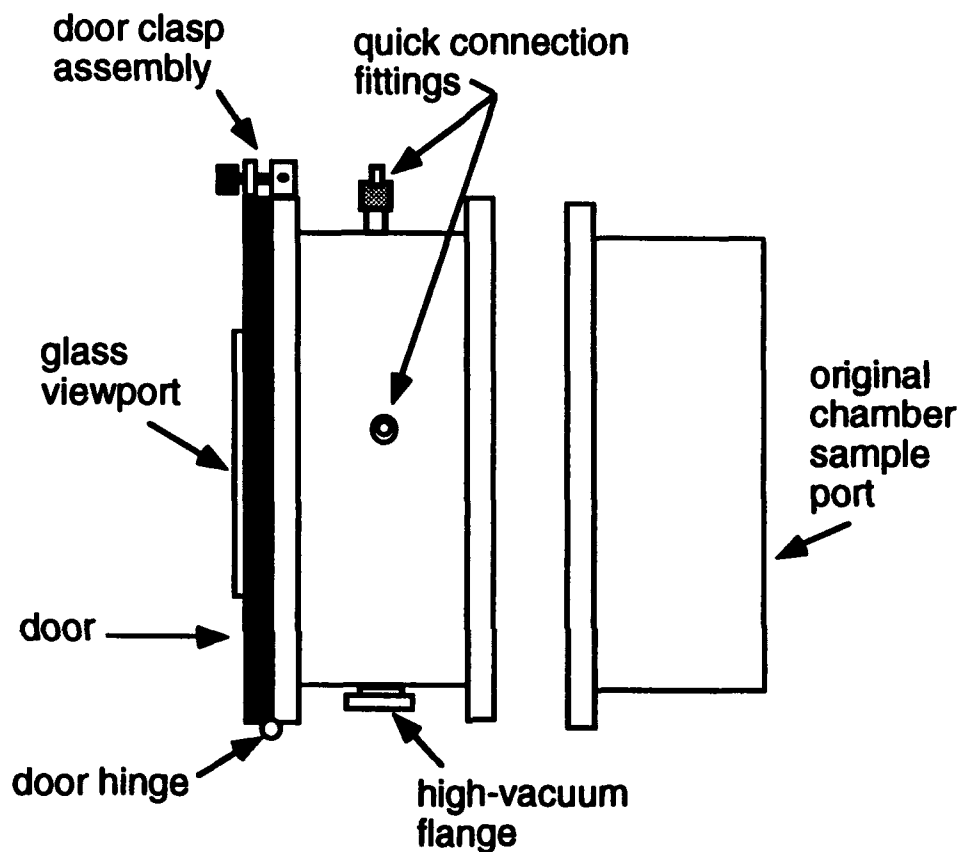


Figure 2. Schematic Diagram of the Chamber Sample Port Extension Assembly.

B. MATERIALS

1. CTFE.

The CTFE used in this study was obtained from the Toxic Hazards Division, Armstrong Aerospace Medical Research Laboratory, Wright-Patterson AFB, OH. It was transferred to a Teflon[®]-capped glass vial and used without further purification. CTFE is also known as 3.1 oil because of its viscosity index. It is a mixture of oligomers of the general formula $\text{Cl}-(\text{CF}_2\text{CFCl})_n-\text{Cl}$. It has been shown by GC/MS studies that CTFE (3.1 oil formulation) is a mixture of two

primary groups, a trimer with a 6-carbon chain, and a tetramer with an 8-carbon chain (Reference 7). Based on these findings, an approximate molecular weight of 450 grams per mole was used in concentration calculations along with a density of 1.93 grams per milliliter.

2. Methane.

The methane used in this study was Fisher high-purity grade (99.99 percent).

3. Helium.

The helium used was high-purity grade (99.995 percent).

4. Oxygen.

The oxygen used was ultra-high-purity (99.99 percent).

5. Water.

The water used was laboratory distilled water.

6. Corroded Aluminum Plates.

These plates were prepared and stored as described earlier (Reference 15).

C. METHODS AND PROCEDURES

1. Sample Preparation and Introduction.

Samples of CTFE vapor were prepared by injecting liquid CTFE into the chamber manifold through a silicon septum. The manifold heating tapes were turned up to about 150 °C to facilitate evaporation of the CTFE which was then flushed into the chamber with helium. For runs conducted under simulated atmospheric conditions, 150 Torr of oxygen were added to 610 Torr of helium. The mixing fan was operated during the filling process. All runs were made at 760 Torr total pressure in the chamber and at 20 °C (unless otherwise noted)..

Methane was added to some runs as an internal standard. It was added as a 10 cc sample from a gas syringe (1 atmosphere sample pressure) injected into the chamber sample manifold during the chamber fill procedure.

Water was added to the chamber to create 'humid' conditions, i.e., approximately 50 percent relative humidity. This was accomplished by injecting 5 mL of liquid water into the chamber sample manifold, then heating and evaporating the water into the chamber.

Ozone was generated by using a commercial production unit (PCI Ozone Corp., model HC2P-18).

2. FT-IR Spectrometer Operation.

The FT-IR spectrometer used in this study was a Nicolet model 6000C which had been upgraded to model 160SX specifications. It includes a 1280 processor with coprocessor, 256K of 20-bit word memory, 24Mbyte hard drive, 1 Mbyte (8-in) floppy drive, and a Write Once Read Many optical storage accessory (Nicolet Maxtor Model RXT-800S). Unless otherwise noted, spectra were run at 1.0 cm^{-1} resolution using a specially-fabricated mercury-cadmium-telluride A (MCT-A) detector (Infrared Associates Model NB FTIR). The number of coadded scans per spectrum varied from 16 to 256 with 128 being the most common. Spectra were acquired under instrument control using the Nicolet FT-IR control language and the MACRO commands it provides.

Molecular species of interest were monitored by recording their absorption spectra as a function of time. A pathlength of 106 meters was used for most of the study, however, this was shortened to 10 meters during experiments with high CTFE concentrations.

A background spectrum for a particular experiment was obtained by co-adding 1024 instrument scans and storing the result. Subsequently acquired sample spectra were ratioed against this stored background spectrum to give absorbance spectra. A typical experimental run was conducted as follows. Immediately after the chamber was filled to begin an experimental run, the FT-IR spectrometer was placed under software control for automatic data acquisition, processing, storage and plotting. The initial spectrum was acquired within 3-5 minutes after the chamber was filled. Then spectra were acquired at regular intervals thereafter as set by the system control software. The resulting data, including time, species absorbance values, and temperature, were sent to an open computer file and stored in ASCII format for off line processing and plotting. All

of these operations and calculations were handled automatically by the instrument's MACRO software. (See Appendix A for a data acquisition flow diagram, and Appendix B-I for data acquisition and processing software program listings.)

3. Ozone Generator Operation.

The ozone generator was operated by passing pure oxygen through it at a flow rate of about 50 standard cubic feet per hour, switching on the power, turning up the 'ozone output' control to an appropriate setting (usually 15-50 percent of full scale) and allowing the ozone-oxygen mixture to flow into the chamber. Then the 'ozone output' control was turned to zero and the power to the ozone generator was shut off while the oxygen was allowed to run for another 30-60 seconds to sweep out any residual ozone and prevent its escape into the lab.

4. RGA Operation.

The RGA system was operated by recording a background spectrum with the chamber empty, using the two most sensitive data acquisition settings and the atmospheric pressure sampling inlet. [The high-vacuum inlet was only used to check the chamber for leaks, but was not very effective for reasons which are not clear at this time]. Once the chamber was filled for an experimental run, another sample was taken. The RGA system was controlled by an external 386SX computer which used Hiden Analytical Ltd. mASYST® software to log and manipulate the resulting data.

5. CTFE Infrared Spectrum.

The infrared spectrum of CTFE is dominated by strong C-X stretching bands ($X = \text{Cl}, \text{F}$) in the $800 - 1300 \text{ cm}^{-1}$ region (Reference 16). The spectrum, acquired at 1.0 cm^{-1} , is shown in Figure 3 with the principal peak positions labeled. The most intense peak, at 1205.8 cm^{-1} was used for quantitation of CTFE during experimental runs.

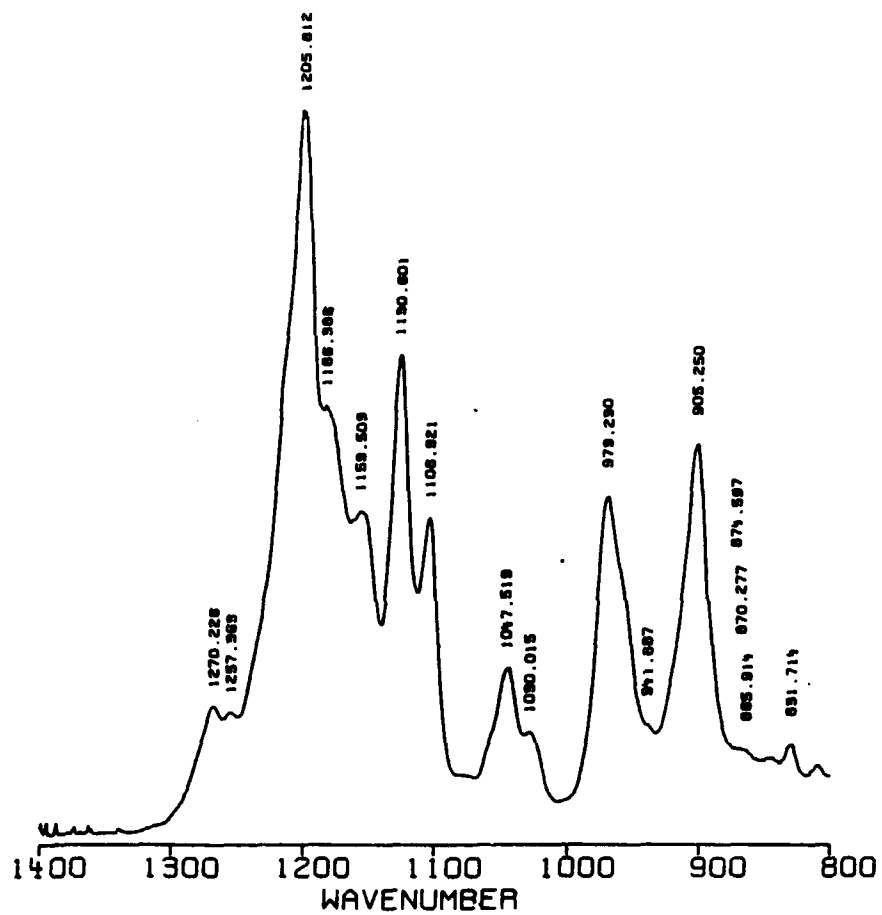


Figure 3. CTFE Infrared Spectrum, 1.0 cm⁻¹ Resolution, with Major Peaks Labeled.

SECTION III

RESULTS AND DISCUSSION

A. CHARACTERIZING CTFE REACTIVITY IN THE CHAMBER WITH NO ADDED PLATES

The experiments conducted in the empty chamber are discussed in chronological order in the following subsections.

1. CTFE in Dry Helium

Since CTFE is a fully halogenated species, its vapor-phase reactivity was expected to be essentially zero. However, experiments with other species in the chamber have shown that adsorption to chamber walls is a major factor in their long-term stability, even under 'inert' conditions. This also proved true of CTFE.

Liquid CTFE (25-35 microliters) was injected into the heated chamber manifold and vaporized then flushed into the chamber with dry, pure helium. The concentration in the chamber ranged from 5-7 parts-per-million (ppm). The CTFE concentration was monitored for 12 days during which time there was a gradual decrease as shown in Figure 4. There was no sign of any reaction or product formation.

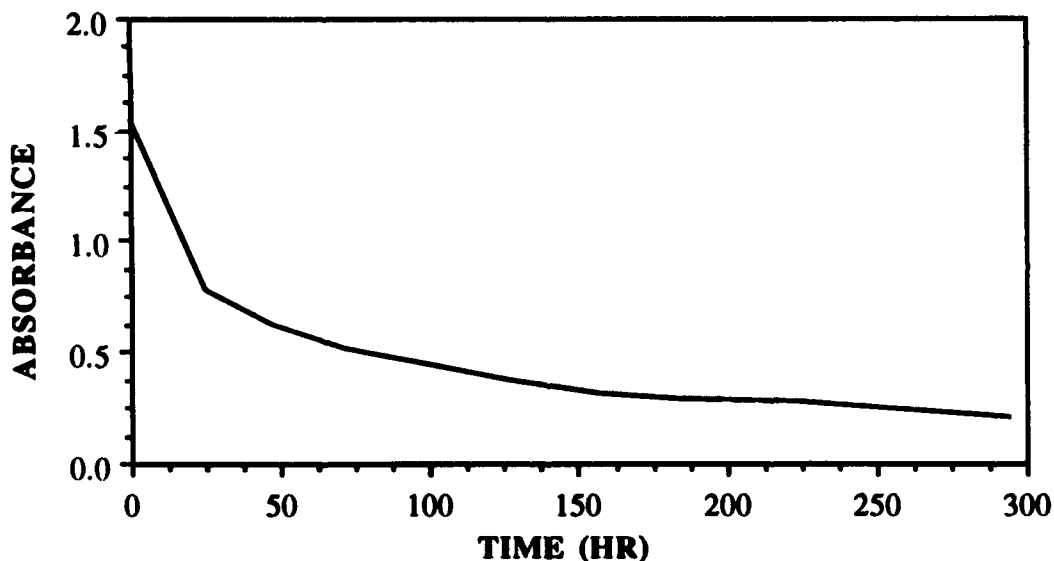


Figure 4. CTFE Decay in Pure, Dry Helium in the Spherical Chamber.

2. CTFE in 20 Percent Oxygen - 80 Percent Helium

Once the initial stability curve had been qualitatively observed, this run was conducted to determine the potential reactivity of CTFE in a synthetic air atmosphere. During the course of the experiment, a new band formed in the 940-1060 cm^{-1} region which appeared to be a reaction product. However, its identity could not be ascertained immediately. The decay of CTFE and the formation of this new band are shown in Figure 5.

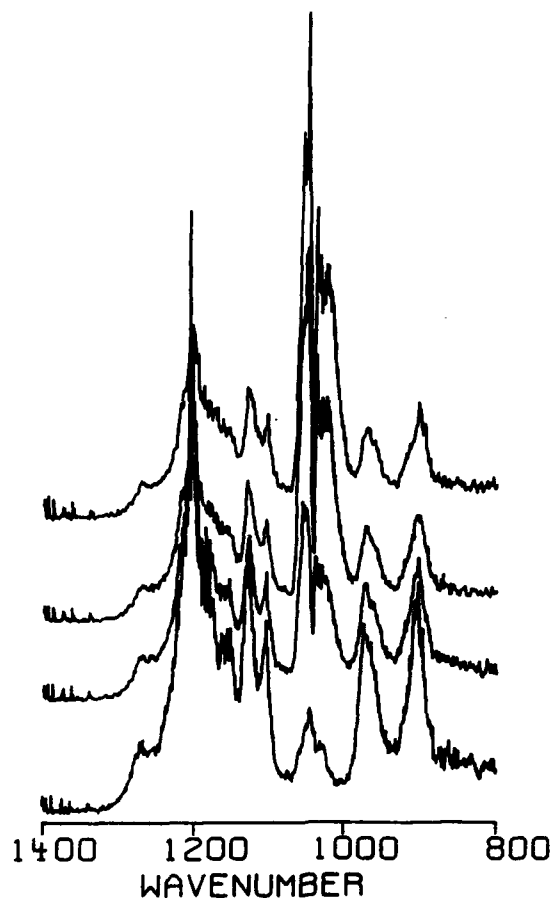


Figure 5. CTFE in 20 Percent Oxygen - 80 Percent Helium in the Spherical Chamber. A Series of Spectra Showing the Formation of a New Species.

After this initial run in synthetic air, the chamber was pumped out for three weeks. Then an experiment was conducted to see if there was any evidence for CTFE offgassing from the chamber

walls. There was only some residual carbon monoxide and nitrous oxide, species which have been observed in the chamber before under similar experimental conditions (Reference 15).

Two sequential runs with CTFE in 20 percent oxygen - 80 percent helium were then conducted. The same "product" band was observed in these runs, strengthening the conclusion that some type of surface-catalyzed reaction was occurring in this system.

Following these runs, the chamber was evacuated overnight with the diffusion pump and liquid nitrogen trap in line. The next day the chamber was filled with 20 percent oxygen and 80 percent helium and then monitored for offgassing products for seven days. The formation of CTFE is shown graphically in Figure 6. The previously observed "product" band ($940\text{-}1060\text{ cm}^{-1}$) was observed, along with small amounts of CTFE, formic acid, and carbon monoxide. These results are shown in infrared spectrum plotted in Figure 7.

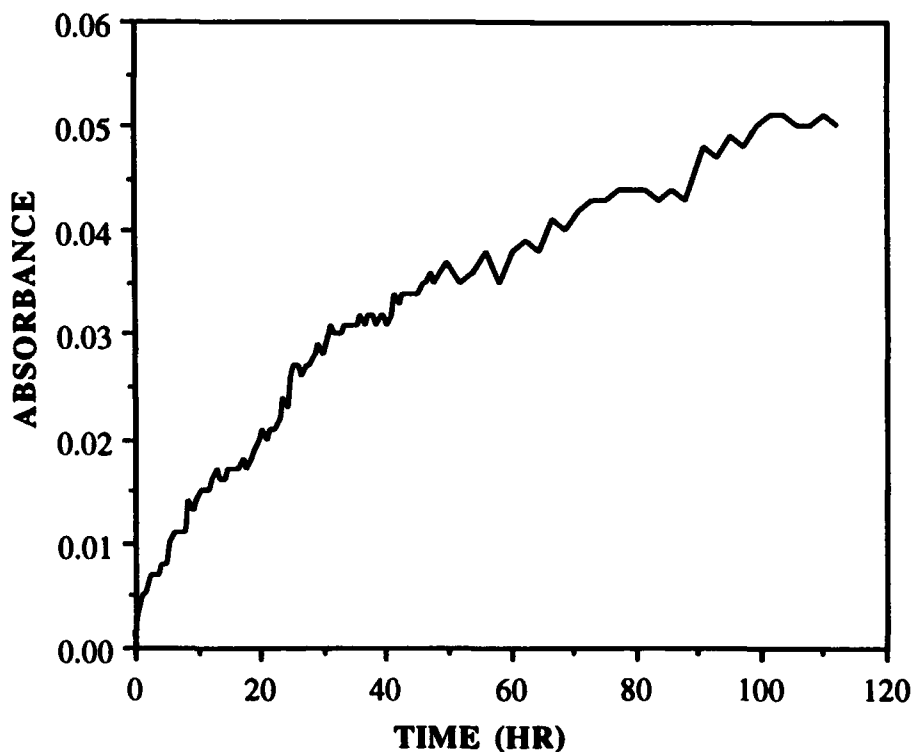


Figure 6. Chamber Desorption Experiment following the CTFE in Synthetic Air Runs Showing CTFE Formation.

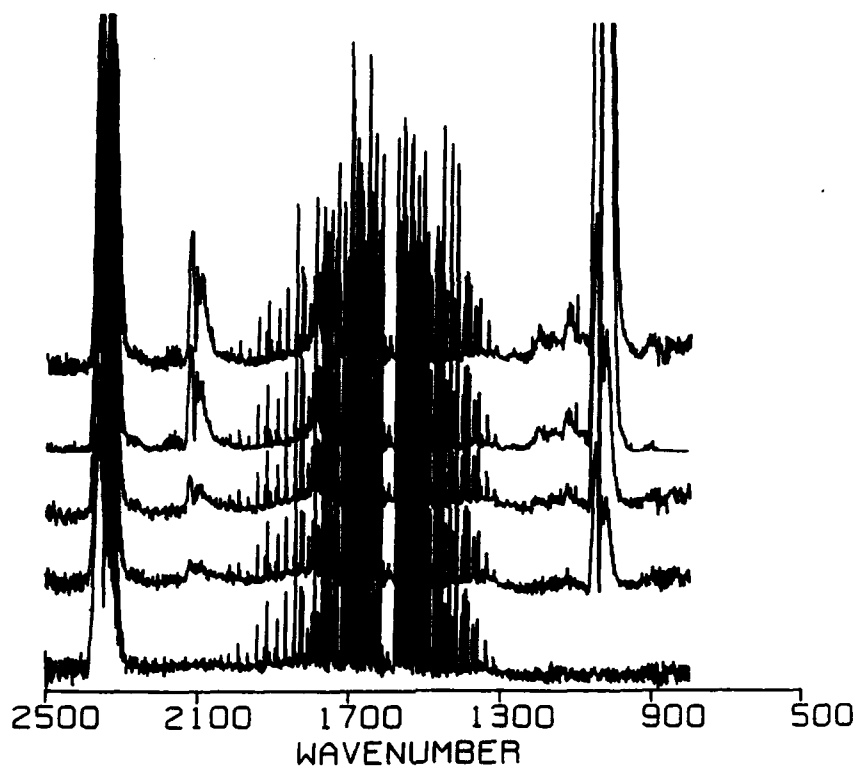


Figure 7. Chamber Desorption Experiment following the CTFE in Synthetic Air Runs Shows Spectra Acquired over a Seven-Day Period.

Another set of experiments was conducted where CTFE was first placed in dry helium and then in a 20 percent oxygen - 80 percent helium atmosphere. In the absence of oxygen, there was only gradual decay of the CTFE with no "product" formation. When oxygen was present, the same "product" band formed.

During the course of these experiments in the empty chamber, the RGA unit was used in an attempt to provide an additional analytical monitor for gaseous chamber species. The sensitivity of the unit proved to be very poor under the conditions of a typical experiment. In other words, with concentrations in the ppm range and pressures near 760 Torr, concentrations of minor species were too low to be seen with the RGA (future plans had included using a jet separator to enrich the samples and increase the instrument sensitivity). Because of this problem, one set of experiments was conducted where the CTFE concentration was increased by a factor of 10 and methane was added as an internal standard. Typical RGA plots are shown below for the empty chamber (Figure 8) and for the chamber with 60 ppm of CTFE and 200 ppm methane (Figure 9).

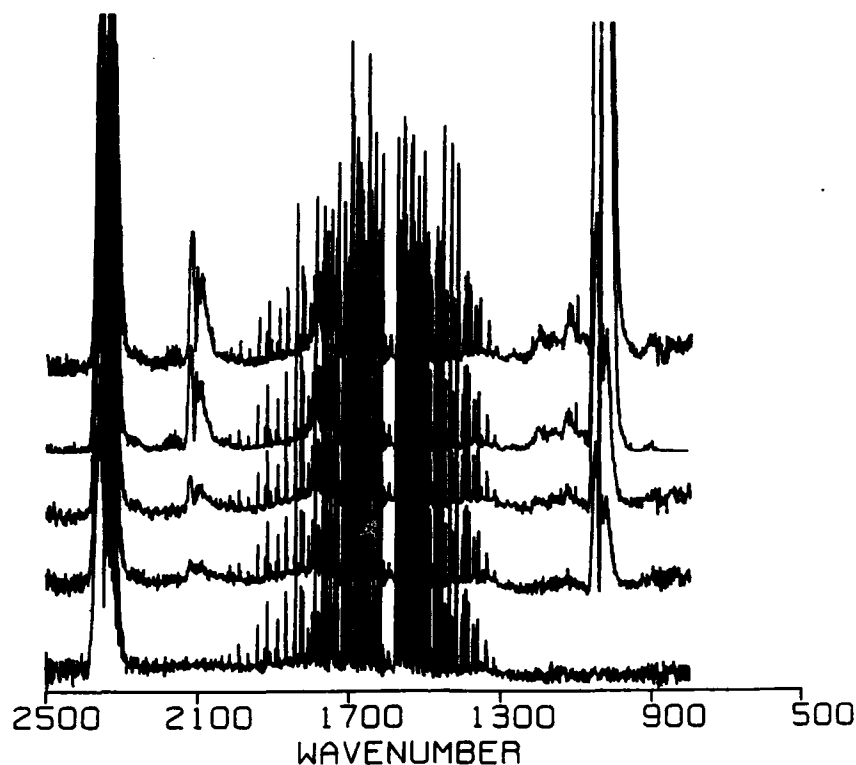


Figure 7. Chamber Desorption Experiment following the CTFE in Synthetic Air Runs Shows Spectra Acquired over a Seven-Day Period.

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After these experiments, the chamber was pumped out for six weeks and then filled with pure air and monitored for any desorption activity. A small amount of CTFE (about 1-2 percent of the original amount injected) was observed to desorb from the chamber. However, none of the "product" was observed.

3. Ozone Experiments

Next, a set of experiments was conducted to determine the potential for surface-catalyzed reactions between ozone and CTFE. The first step in this procedure was to see if ozone was stable in the chamber. This was followed by additional runs to see if there was any baseline (i.e., empty chamber) reactivity between ozone and CTFE. Approximately 25-50 ppm ozone were introduced into the chamber (based on an absorptivity of $9.7 \text{ cm}^{-1}\text{atm}^{-1}$, base e, for the band at 1055 cm^{-1} [Reference 17]) in dry helium. After 4 days in the chamber, the ozone had decayed to about one fourth of its original value and some formic acid had formed (some CTFE desorption was also evident). The formic acid is visible in Figure 10 which is the ozone spectrum after 4 days minus 1.52 times the original ozone spectrum.

Observation of the ozone spectra quickly led to another interesting conclusion: the "product" peak in the earlier CTFE runs in oxygen and helium was ozone. The mechanism for its production is not clear, but must involve a surface-catalyzed process of some type.

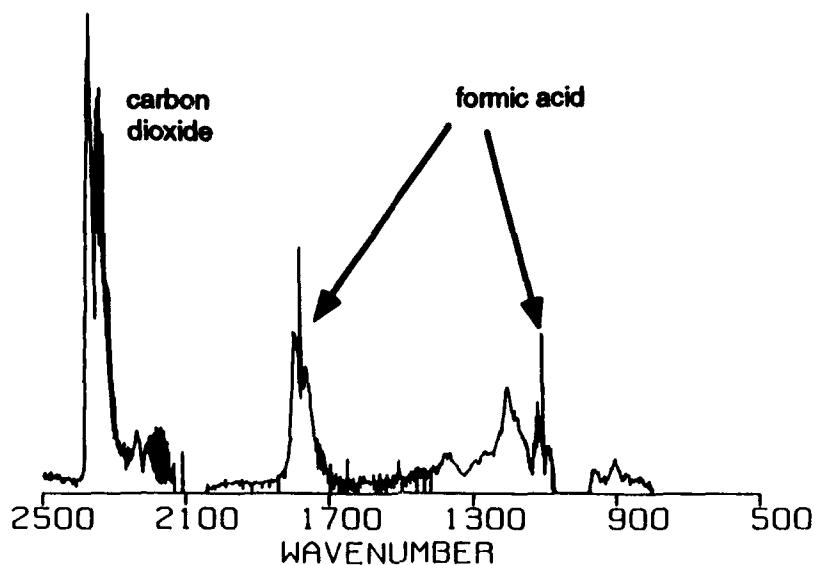


Figure 10. Formic Acid from the Decay of Ozone in the Spherical Chamber

The chamber was pumped out and 5 ppm CTFE were added in 750 Torr of dry helium. Then 10 Torr of oxygen were added with the PCI ozone generator was turned on long enough to produce about 25 ppm ozone. Then the reaction was followed for about 8 days. The ozone decayed in a nearly linear fashion for the first 4 days, then abruptly began to increase. The increase continued through the remainder of the run. This behavior was not expected, but appears to be another case of surface-catalyzed ozone production. The mediator for this process must be CTFE, because in earlier runs in this same chamber with hydrazine, this ozone production phenomena was never observed.

The CTFE decayed more rapidly in the presence of ozone. However, it showed the same general pattern of decay -- a faster rate for the first few hours, followed by a slower rate for the remainder of the run. The CTFE and ozone time-concentration curves are shown in Figure 11. Even though the decay rate was more rapid in the presence of ozone, there was no evidence, in terms of discernable product formation, that any specific chemical reactions had occurred. The reason for the increase in decay rate is not clear at this time.

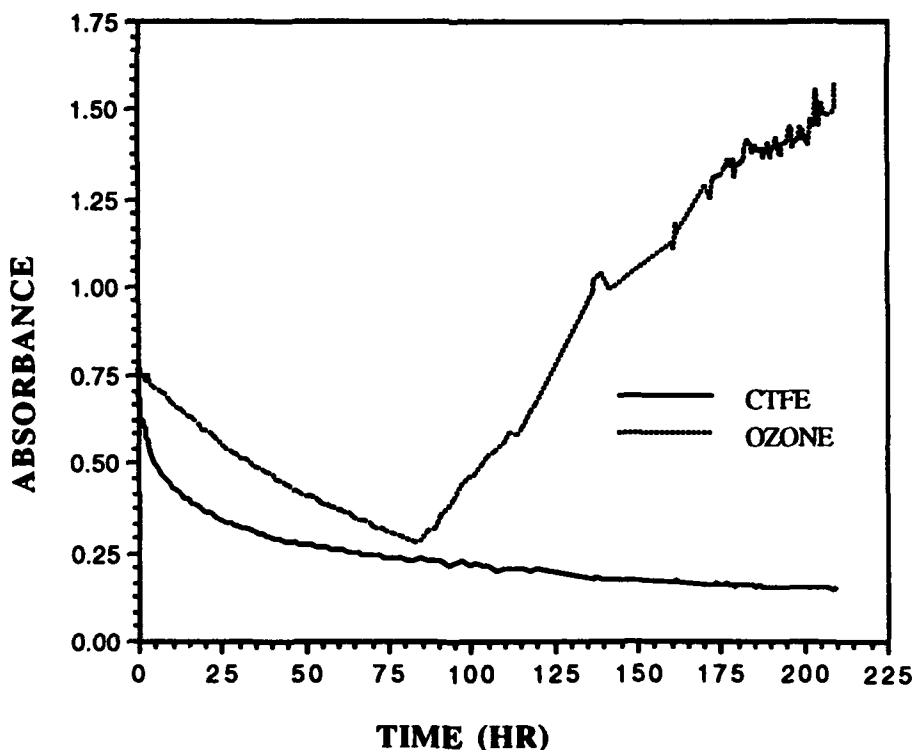


Figure 11. Plot of CTFE and Ozone Concentrations with Time.

4. High-Humidity Experiments

To test the effects of humidity on the decay of CTFE in the empty chamber, a run was conducted at about 50 percent relative humidity in helium. Five milliliters of water were vaporized into the chamber and flushed in with helium. Then 5 ppm CTFE were vaporized and flushed in with helium. Then the system was monitored for 4 days. The CTFE decayed more rapidly than it had done in dry helium; the decay rate was about the same as when ozone was present.

The relative decay rates of the CTFE under different experimental conditions can best be compared by viewing the normalized decay curves on a common plot. This is shown in Figure 12.

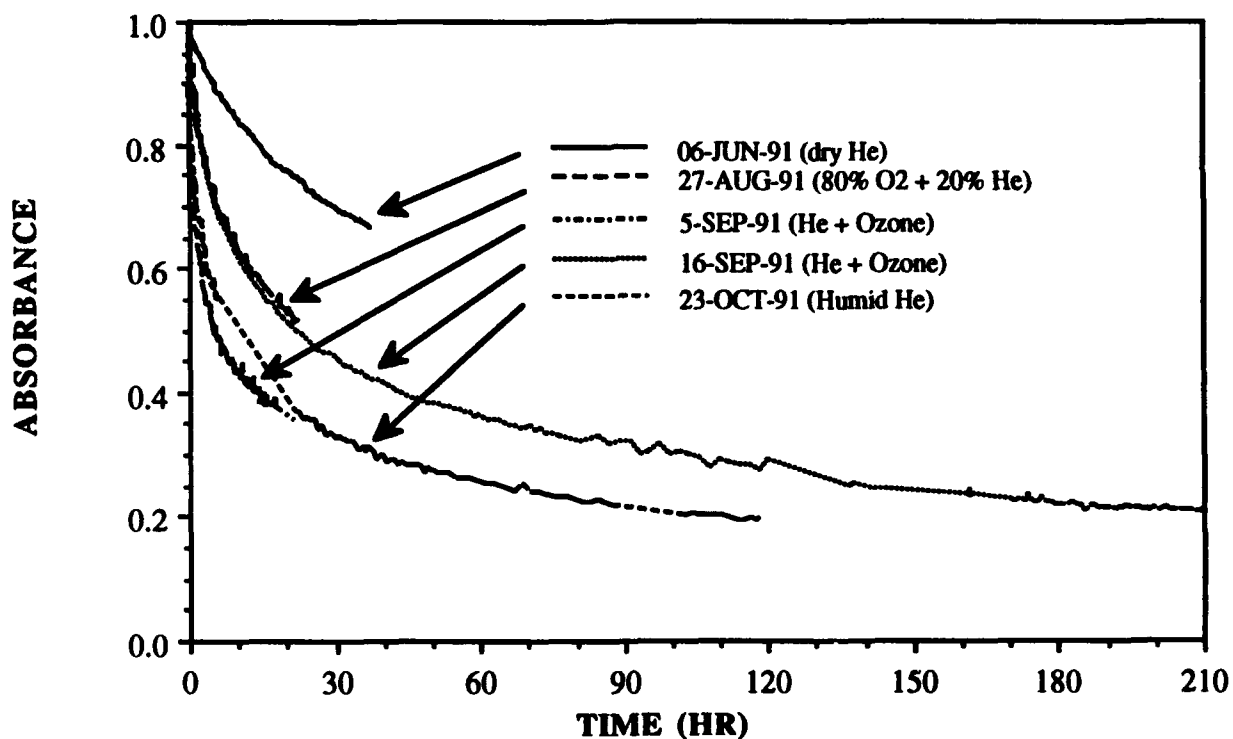


Figure 12. Normalized CTFE Decay Curves.

B. CHARACTERIZING CTFE REACTIVITY IN THE CHAMBER WITH 20 ADDED CORRODED ALUMINUM PLATES

1. Overview Tests

When the 20 corroded aluminum plates (the same ones which were used in the hydrazine experiments described in Reference 15) were added to the chamber, they were first isolated and observed to be sure they were not offgassing any vapors from previous experiments with hydrazine. There was no sign of any offgassing.

The overview tests were commenced with the introduction of 5 ppm of CTFE into the chamber in 760 Torr of dry helium. By the time the CTFE was introduced (about five minutes), it was nearly all adsorbed. The small amount which remained decayed away within three to four hours.

To compare with earlier experiments on hydrazine, the chamber was pumped down to 500 Torr, then 5 milliliters of water were vaporized and flushed in with helium to see if CTFE would be desorbed from the plates and reappear in the gas phase. About 25 percent of the original CTFE was desorbed and appeared in the infrared spectrum. Once desorbed, it decayed slowly. This behavior is similar to that displayed by hydrazine and typical of chemical species which have a high affinity for surfaces.

Finally, the chamber was pumped to 610 Torr and oxygen was added. There was no dramatic increase in decay rate and no evidence for any ozone production.

2. Ozone Experiments

Finally, a run was conducted where the chamber was filled to 400 Torr with dry helium, then 5 ppm CTFE were vaporized and flushed in with helium to 740 Torr. Then ozone was produced as the chamber was brought to 760 Torr by the addition of pure air. The initial aliquot of CTFE was rapidly adsorbed, so after about 10 minutes, the chamber was pumped out to 650 Torr and another 5 ppm were injected and flushed in. The CTFE decayed rapidly, reaching a concentration of essentially zero in about 30 minutes. The ozone also decayed rapidly and was gone within about 2.5 hours. No obvious reaction products were observed.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

A. NO ADDED PLATES

Although the chamber is Teflon® coated, CTFE decay, when no test plates were added, was still controlled by surfaces present inside including the walls, mirrors, and other external ports and openings. This surface adsorption is essentially irreversible under dry conditions, i.e., there is very little desorption of CTFE after the chamber is exposed to it.

When 20 percent oxygen is added to the helium, the decay proceeds somewhat more rapidly and ozone forms, probably from surface-catalyzed processes. The spontaneous formation of ozone is unusual because of the highly reactive nature of this species.

When ozone was specifically generated, it reacted with CTFE causing the CTFE to decay somewhat more rapidly than was the case when no ozone was present. However, no specific reaction products could be detected suggesting that the ozone serves to promote surface loss processes which remain adsorbed.

In the presence of large water concentrations (i.e., runs conducted under humid conditions), the decay of CTFE occurred at about the same rate as when ozone was present under dry conditions. Again, no major reaction products were formed, indicating that the increased rate was restricted to surface activity.

The observed behavior generally supported the expectation that CTFE would be unreactive in the vapor phase with respect to homogeneous processes. Its disappearance in the chamber can be attributed solely to surface adsorption processes, some of which are enhanced by the presence of water or ozone.

B. CORRODED ALUMINUM PLATES

These plates were added because they represented the most reactive surface from earlier experiments with hydrazine (Reference 15). Thus it was felt that if any surface-catalyzed reactions

were going to be observed with CTFE, they would probably occur with these plates. This proved not to be the case. The only effect of the plates was to enhance the rate of the adsorption processes because of the significant increase in available surface area. There were no new vapor-phase species produced by surface-catalyzed chemical reactions. The only other difference observed with the plates present was that no ozone was produced when CTFE was introduced into the chamber with dry helium and oxygen.

C. RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The experiments summarized in this report represent only a portion of those which were originally planned. Thus, there were only able to partially address the reactivity of CTFE in the atmosphere. These studies were able to show, however, that CTFE is probably chemically unreactive toward surfaces under dark conditions. The main loss process appears to be surface adsorption. There is some risk associated with CTFE desorption, especially after repeated spills to the same area.

The one area which requires additional research is that of photochemical reactions occurring on surfaces. There is strong evidence from earlier researchers (References 11 and 12) that the combination of sunlight and soil particles (and perhaps other surfaces such as concrete, asphalt, and metals) could cause the photochemical breakdown of CTFE.

To accomplish photolysis studies in the spherical chamber will require the installation of the Pyrex® immersion well shown schematically in Figure 13. The well was designed to accept a 2.5 kilowatt, high-pressure xenon arc lamp and provide radiation inside the chamber in the 290 - 700 nanometer range. The details of the required lamp cooling system remain to be worked out, but the lamp manufacturer felt that the proper arrangements could be made (Reference 18). There are Teflon®-coated aluminum pans available for use in the chamber which could serve as sample holders. Such tests could show whether surface-catalyzed photolysis processes could play a role in the environmental fate of CTFE.

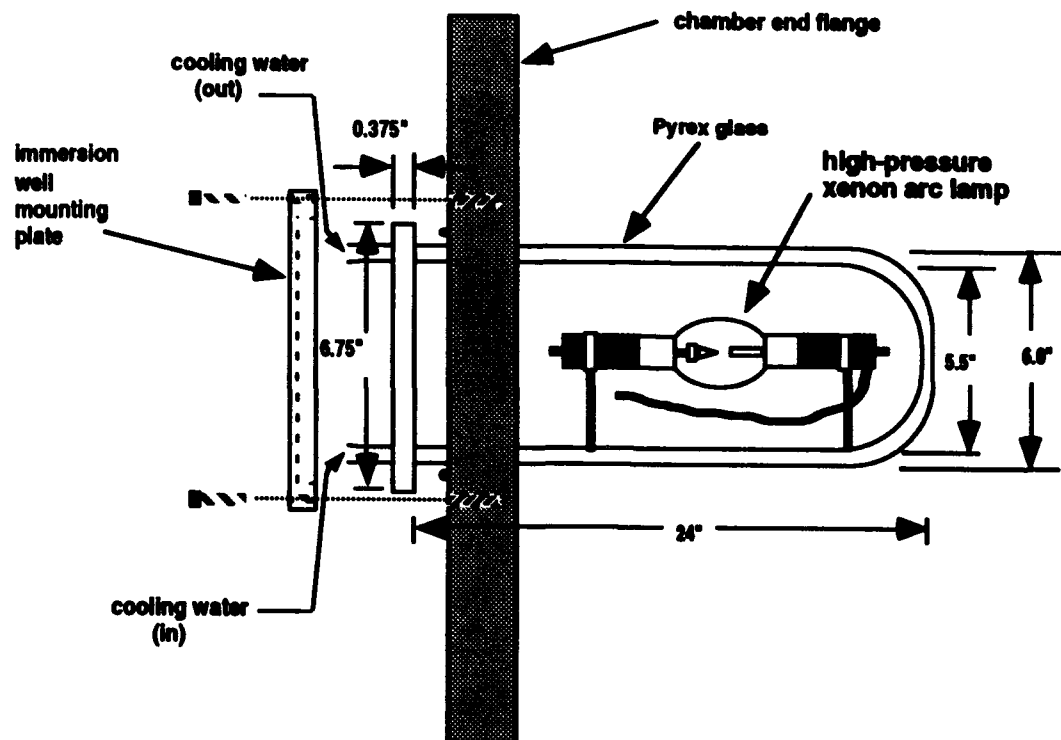


Figure 13. Schematic Diagram of Immersion Well for High-Pressure Xenon Arc Lamp.

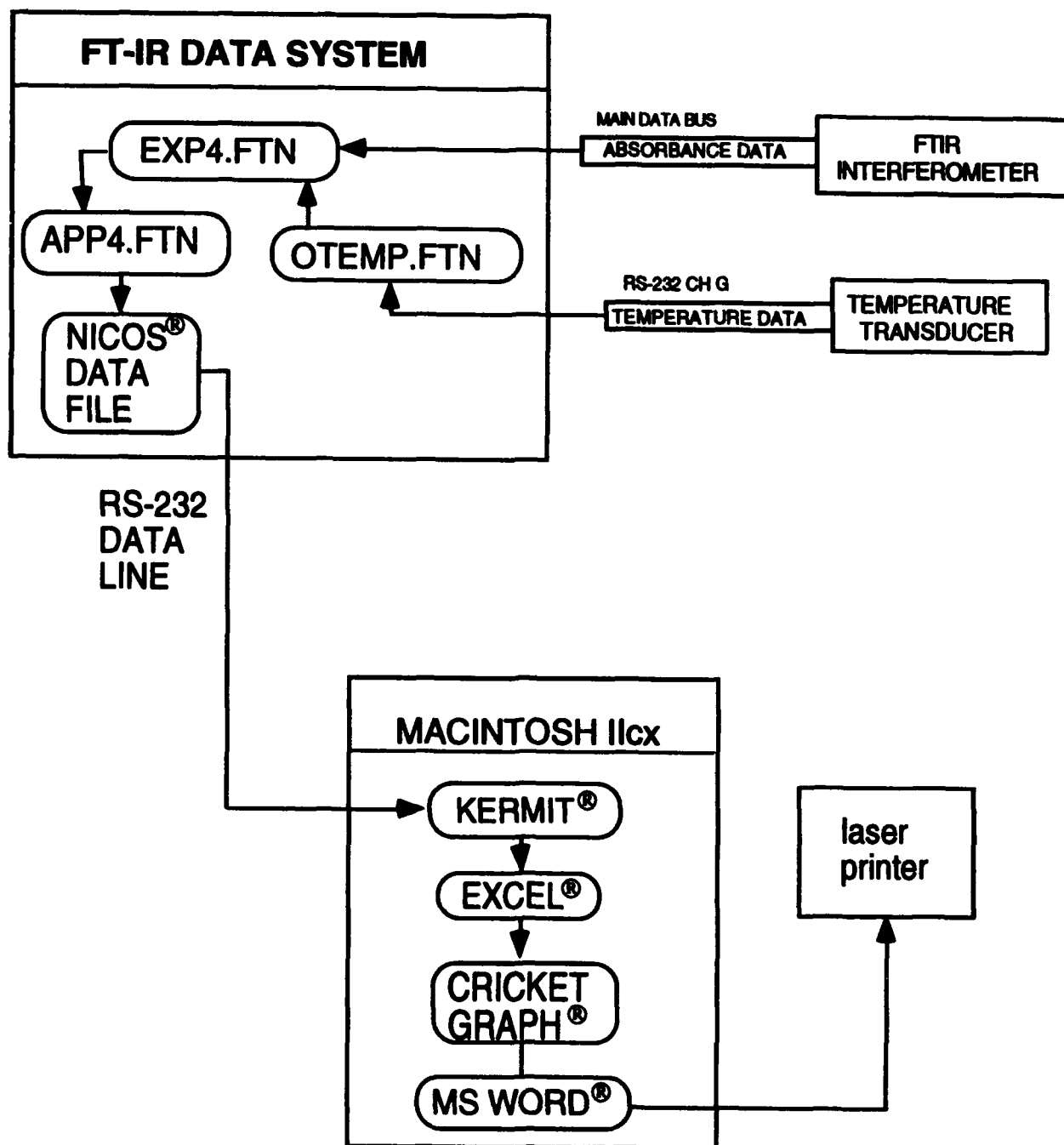
REFERENCES

1. J. S. Smith, Corosion and Lubricity Testing of Nonflammable USAF Formulated CTFE Base Hydraulic Fluid, Report No. 2473, Belvoir RD&E Center, Materials, Fuels & Lubricants Dir., Fuels & Lubricants Division, Ft Belvoir, VA, September 1988.
2. V. K. Gupta, L. J. Gschwender, C. E. Snyder, Jr., and M. Prazak, "Thermal Stability Characteristics of a Nonflammable Chlorotrifluoroethylene CTFE Basestock Fluid," Journal of the Society of Tribologists and Lubrication Engineers, Vol. 46, pp. 601-605, 1990.
3. M. P. Mahony, "A Cost and Benefit Analysis of Hydraulic Fluid Systems for the Next Generations of Tactical Aircraft," Masters Thesis, Air Force Institute of Technology, Air University, September 1987.
4. "Chlorotrifluoroethylene (CTFE) Oils, Greases & Waxes," Halocarbon Products Corp., P.O. Box 833, Hackensack, NJ, 1988.
5. E. R. Kinkead, C. L. Gaworski, J. R. Horton, and T. R. Boosinger, Chlorotrifluoroethylene Oligomer: Evaluation of Acute Delayed Neurotoxicity in Hens and Study of Adsorption and Metabolism in Rats Following Oral, Dermal, and Inhalation Exposure, AAMRL-TR-87-044, AAMRL Toxic Hazards Division, HSD, AFSC, Wright-Patterson AFB, OH, September 1987.
6. E. R. Kinkead, B. T. Culpepper, S. S. Henry, P. S. Szotak, C. D. Flemming, R. S. Kutzman, R. H. Bruner, J. R. Wyman, and D. R. Mattie, The Determination of the Acute and Repeated Oral Toxicity of Halocarbon Oil. Series 27-S, AAMRL-TR-89-007, AAMRL Toxic Hazards Division, HSD, AFSC, Wright-Patterson AFB, OH, February 1989.
7. E.R. Kinkead, B. T. Culpepper, S. S. Henry, V. L. Moroughan, E. C. Kimmel, D. L. Pollard, C. D. Flemming, H. G. Wall, H. F. Leahy, R. S. Kutzman, R. B. Conolly, A. Vinegar, R. E. Whitmire, and D. R. Mattie, Subchronic Studies of Chlorotrifluoroethylene, AAMRL-TR-89-021, AAMRL Toxic Hazards Division, HSD, AFSC, Wright-Patterson AFB, OH, June 1989.
8. E. R. Kinkead, B. L. Culpepper, S. S. Henry, P. S. Szotak, C. D. Flemming, R. S. Kutzman, R. H. Bruner, J. F. Wyman, and D. R. Mattie, "The Determination of the Repeated Oral Toxicity of Halocarbon Oil, Series 27-S," Toxicology and Industrial Health, Vol. 6, pp. 17-32, 1990.
9. D. A. Stone, A Controlled-Environment Chamber for Atmospheric Chemistry Studies Using FT-IR Spectroscopy, ESL-TR-89-44, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, FL, June 1990.
10. D. A. Stone, "A Controlled-Environment Chamber for Atmospheric Chemistry Studies Using FT-IR Spectroscopy", Applied Spectroscopy, Vol. 44, pp. 945-950, 1990.
11. S. Gaes, J. Schmitzer, H. W. Thamm, H. Parlar, and F. Forte, "Photomineralization Rate of Organic Compounds Adsorbed on Particulate Matter," Nature, Vol. 270, pp. 331-333, 1977.
12. P. Ausloos, R. E. Rebbert, and L. Glasgow, "Photodecomposition of Chloromethanes Adsorbed on Silica Surfaces," JOURNAL OF RESEARCH of the National Bureau of Standards, Vol. 82, pp. 1-8, 1977.

13. J. U. White, "Long Optical Paths of Large Aperture," Optical Society of America, Vol. 32, pp. 285-288, 1942.
14. W. B. Olson, "Minimization of Volume and Astigmatism in White Cells for Use with Circular Sources and Apertures," Applied Optics, Vol. 23, pp. 1580-1585, 1984.
15. D. A. Stone and J. R. Long, Hydrazine Decay in the Atmosphere: Controlled-Environment Chamber Studies and Kinetic Modeling, ESL-TR-91-34, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, FL , July 1991.
16. L. J. Bellamy, The Infra-red Spectra of Complex Molecules, Chapter 19, Chapman and Hall, London, 1975.
17. E. C. Tuazon, A. M. Winer, R. A. Graham, J. N. Pitts, Jr., Atmospheric Measurements of Trace Pollutants: Long Path Fourier Transform Infrared Spectroscopy, EPA/600/09, Final Report 6/76 - 5/80, Research Triangle Park, NC, March 1981.
18. R. Sweet and R. Jackson, Optical Radiation Corp., 1300 Optical Dr., Azusa, CA 91702, personal communication, 1991.

APPENDIX A

FLOW DIAGRAM FOR DATA ACQUISITION AND ANALYSIS



APPENDIX B

SOFTWARE LISTING FOR THE PROGRAM USED FOR OVERALL CONTROL OF FT-IR DATA ACQUISITION AND STORAGE

This program is called CT4. It was written in the Nicolet MACRO language by using the text editor called TED. It was then compiled into a form compatible with the FT-IR software by using a Nicolet program called MACCRT. The use of the text editor allows comments to be included in a MACRO program for documentation and user assistance.

The main MACRO program (CT4) calls other SUB-MACRO programs. There were written and compiled as subsections of CT4. Each program ends with the statement END. Each new subsection begins with "!" followed by the program name.

```
!CT4
BFN
DFN
VI2=0
NSD
OMD
ENTER EXCEL FORMAT DATE  (DETERMINE BY RUNNING DATEME.FTN IN
                           NICOS)

RTP
OMD
THE CURRENT SPECIES TO BE MONITORED ARE: CTFE, CH4, H2O, AND
                                           O3

WTY=1
SMN=1
SIZ=1
ITR=1
MNT=0
RTO=0
OMD
ENTER THE DELAY TIME (IN MIN) BETWEEN SPECTRA
VI3
OMD
PRESS "RETURN" TO BEGIN
PAU
VI0=0
CT7
END

!CT7
FOR AAA=1 TIL 120
CT8
DFN=DFN+1
DCL=204445
DCX
GFN
```

TIME2.FTN *(FORTRAN PROGRAM TO EXECUTE THE TIME DELAY)*
FRN
DCL=210414
DCX
NXT AAA
END

!CT8
SCD
GFN
OTEMP.FTN *(FORTRAN PROGRAM TO ACQUIRE TEMPERATURE DATA)*
FRN

OFN=DFN
MOS
RAS
ABS
XSP=4000
XEP=700
YSP=-.25
YEP=1.25
DSS
XEP=0
DFN=SFN
VI2=VI2+1

GFN
EXP4.FTN *(FORTRAN PROGRAM TO ACQUIRE ABSORBANCE DATA)*
FRN

GFN
APP4.FTN *(FORTRAN PROGRAM TO STORE ABSORBANCE DATA)*
FRN

DFN=OFN
END

[NOTE: statements in italics are comments only, not a part of the actual program]

APPENDIX C

SOFTWARE LISTINGS FOR THE FORTRAN PROGRAM USED TO CONTROL DATA ACQUISITION TIMING FROM 1280 DATA SYSTEM CLOCK

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C TIME2.ASC          PROGRAM TO RETRIEVE TIME (IN SEC FROM      C
C                    MIDNIGHT) FROM LOCATION 071 OF PAGE ZERO  C
C                    MEMORY AND USE TO CONTROL THE INTERVAL    C
C                    BETWEEN SETS OF FT-IR SCANS.              C
C                                                            C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C234567

```

```

      INTEGER TIM
      INTVL=IRVAL(13765,0)
      ICOUNT=60*INTVL
      IFLAG=0
      IFLAG2=0
      ISUM=0

C
C  INITIALIZE THE TIME COUNTER (TIM)
C
A  .ZERADD IS0 71
A  MEMA IS0
      TIM=IS0

C
C      WRITE(2,12) INTVL,ICOUNT,IFLAG,TIM
C 12      FORMAT(' ', 'INTVL=', I4, 2X, 'ICOUNT=', I4, 2X, 'IFLAG='
C      :      , I4, 2X, 'TIM=', I6, /)

      30  CONTINUE

A  .ZERADD IS0 71
A  MEMA IS0

C      IF (IS0 .GT. TIM) PRINT*, 'IS0=', IS0
      IS3=IS0
C      PRINT*, 'IS3=', IS3
      IF (IS3 .EQ. 16) IFLAG2=1
C      IF (IFLAG2 .EQ. 1) PRINT*, 'IFLAG2=', IFLAG2
      IF (IFLAG2 .EQ. 1) IS3=IS3+86400
C      PRINT*, 'IFLAG2=', IFLAG2, 'IS3=', IS3, 'ISUM=', ISUM
      IF (IFLAG2 .EQ. 1 .AND. (ISUM-IS3) .LE. 0) CALL EXIT
      IF (IFLAG2 .EQ. 1) GOTO 30

      IF (IFLAG .EQ. 0) ISUM=IS3+ICOUNT

C      PRINT*, 'ISUM=', ISUM, 'IS3=', IS3,

```

```
      IF ((ISUM-IS3) .LE. 0) CALL EXIT  
      IFLAG=1  
      GOTO 30
```

```
END
```

BATCH FILE USED TO COMPILE THE ABOVE PROGRAM.

NAME: TIME2.BAT

LISTING

```
RUN FORTRAN  
TIME2.ASC:L  
RUN RELOAD  
:B=1000-53777  
TIME2.REL:L  
IRVAL.REL [ROOT,HLIB]:L  
FORRUN.LIB [ROOT,HLIB]:R  
NICAPL.LIB [ROOT,HLIB]:R  
DPSYS.LIB [ROOT,HLIB]:R  
FIOS.LIB [ROOT,HLIB]:R  
NICSYS.LIB [ROOT,HLIB]:R  
/-TT:U  
/TIME2.FTN:S  
DEL TIME2.REL  
DEL TIME2.TMP
```


APPENDIX D

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO READ AND REPORT THE CHAMBER TEMPERATURE

```

C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      PROGRAM OTEMP.ASC
C
C      THIS IS A PROGRAM TO READ ASCII TEMPERATURE DATA
C      FROM AN OMEGA MODEL 680 THERMOCOUPLE THERMOMETER
C      INTO THE FT-IR DATA SYSTEM AND STORE THE RESULT IN
C      EACH SCRATCH FILE STATUS BLOCK IN LOCATIONS 68-71.
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C  DEFINE VARIABLES
      INTEGER CHANNEL, BAUDRATE, BIT, BAUDVAL, DELAY, IOUT, I,
      1DELTA, VALUE
      LOGICAL VALID
      CHARACTER*10 TMP(10), WT, CONC
      CHARACTER*1 CHR, T1, T2, T3, T4, T5, T6, T7, T8
C  SET BAUDRATE AT 1200, CHANNEL=2 (I.E., CHANNEL G)
C  AND CALL SUBROUTINE BAUDSET
      BAUDRATE=1200
      CHANNEL=2
      VALID =.TRUE.
C      PRINT *, 'CALLING BAUDSET'
      CALL BAUDSET(CHANNEL, BAUDRATE, VALID)

C  SEND CHARACTER "R" TO REQUEST DATA TRANSMISSION FROM THE
C  OMEGA UNIT
      VALUE = 82
C      PRINT *, 'CALLING CHWRITE'
      CALL CHWRITE (CHANNEL, VALUE, VALID)

C  RECEIVE THE CHARACTERS TRANSMITTED BY THE OMEGA UNIT
      DELAY=0
      DO 10 I=1,8
          CALL CHREAD(CHANNEL, DELAY, CHR, VALID)
C          PRINT *, 'I=', I
          TMP(I)=CHR
C          PRINT *, 'TEMP=', TMP(I)
      10  CONTINUE
C      DO 20 I=1,8
C          WRITE(3,100) I, TMP(I)
C100  FORMAT(' ', 'I=', I2, 2X, 'TEMP=', I4)
C20  CONTINUE

      T1=TMP(1)

```

```

      T2=TMP(2)
      T3=TMP(3)
      T4=TMP(4)
      T5=TMP(5)
      T6=TMP(6)
      T7=TMP(7)
C     T8=TMP(8)
      WT=T1 // T2 // T3 // T4 // T5 // T6 // T7
C     PRINT *, 'T=', WT, ' DEG C'
      TEMP=REAL(WT)
      RETURN
      END

```

BATCH FILE USED TO COMPILE THE ABOVE PROGRAM.

NAME: OTEMP.BAT

LISTING

```

RUN FORTRAN
OTEMP.ASC:L
RUN FORTRAN
BAUDSET.ASC:L
RUN FORTRAN
CHWRITE.ASC:L
RUN FORTRAN
CHREAD.ASC:L
RUN RELOAD
:B=1000-53777
OTEMP.REL:L
BAUDSET.REL:L
CHWRITE.REL:L
CHREAD.REL:L
IRVAL.REL [ROOT,HLIB]:L
FORRUN.LIB [ROOT,HLIB]:R
NICAPL.LIB [ROOT,HLIB]:R
DPSYS.LIB [ROOT,HLIB]:R
FIOS.LIB [ROOT,HLIB]:R
NICSYS.LIB [ROOT,HLIB]:R
/-TT:U
/OTEMP.FTN:S
DEL OTEMP.REL
DEL OTEMP.TMP
DEL BAUDSET.REL
DEL BAUDSET.TMP
DEL CHWRITE.REL
DEL CHWRITE.TMP
DEL CHREAD.REL
DEL CHREAD.TMP

```

APPENDIX E

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO PROCESS AND STORE DATA INTO AN ASCII FILE ON THE NICOLET FOR LATER ANALYSIS AND PLOTTING

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   EXP4.ASC   (gives absorbance values for 4 species)
C   THIS PROGRAM RETRIEVES DATA FROM FT-IR SCRATCH FILES,
C   AND CALCULATES BASELINE-CORRECTED ABSORBANCE VALUES
C   FOR ANALYTICAL PEAKS.  THERE IS A SUBROUTINE FOR EACH
C   SPECIES OF INTEREST.  THERE IS ALSO A SUBROUTINES FOR
C   TEMPERATURE DETERMINATIONS.  A TYPICAL LINE OF OUTPUT
C   DATA WOULD LOOK LIKE:
C
C   32020      08  39  15      20.5      1.034      0.0031      0.537      0.0002
C
C   WHERE THE NUMBERS ARE (IN ORDER)  EXCEL DATE, FT-IR TIME,
C   TEMPERATURE, AND ABSORBANCE VALUES FOR CTFE, CH4, H2O
C   AND O3 RESPECTIVELY.
C
C   THE PROGRAM WAS BEEN MODIFIED TO PRINT ITS OUTPUT TO
C   A FILE CALLED HOLD.DAT.  THIS FILE MUST PREEXIST!
C   THE SINGLE LINE OF DATA IN HOLD.DAT IS THEN READ BY
C   THE PROGRAM APP4.FTN.  APP4.FTN THEN READS THE VALUES
C   FROM THE FILE IROUT.DAT. (NOTE!  IROUT.DAT MUST BE
C   'INITIALIZED' BY THE FOLLOWING COMMAND PRIOR TO THE
C   START OF AUTOMATED DATA COLLECTION:
C
C           SX>COPY IROUT.HLD>IROUT.DAT
C
C   BEFORE APP4.FTN CAN APPEND NEW VALUES.)  IROUT.HLD
C   CONTAINS A HEADER VALUE OF 1 FOLLOWED BY A LINE OF
C   ZEROES IN THE PROPER FORMAT.  APP4.FTN THEN REWRITES THE
C   VALUES TO THE SAME FILE AND AT THE END WRITES THE VALUES
C   READ FROM THE FILE HOLD.DAT.  PSUEDO FILE APPENDING IS
C   ACCOMPLISHED.
C
C   THE INITIAL CONTENTS OF HOLD.DAT ARE NOT IMPORTANT SINCE
C   IT IS NEVER READ AND IS WRITTEN OVER WITH A SINGLE LINE
C   OF DATA DURING EACH CALL OF THIS PROGRAM.
C
C   PROGRAM DIMENSIONED FOR 1.0 CM-1 SPECTRA
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

```

      REAL      Y(16384),BP1,LBP, PXA, PYA, CABS, XDIF, XDIF2, YDIF,
:             FAC1, FAC2, EP, SP, A1, A2, A3, A4

```

```

INTEGER  IDATA(512),IDA(22528),COUNT,DP1,DP2,
INTEGER  TFLAG,LDATE,NGEN,INCR
CHARATER*2  HH,NN,SS
CHARACTER*1  CT1,CT2,CT3,CT4,C(10)
CHARACTER*1  H1,H2,N1,N2,S1,S2
CHARACTER*4  CTEMP
CHARACTER*64 OUTPUT
CHARACTER*10 DATFIL
INTEGER  I, M, NUMP, MAXPOINTS

```

```

C
C  SET INITIAL VALUES
C

```

```

FLASER = 15798.2
NPMAX = 22528
SN = 0
NGEN = 0
INCR = 1

```

```

C
C *****
C  READ FTIR PARAMETERS FOR DATA RETRIEVAL:
C

```

```

IDFN = IRVAL(14022,0)
NSECS = IRVAL(14001,0)
INODE = IRVAL(13004,0)
NDPW = IRVAL(14000,0)
IXSP = IRVAL(14025,0)
IXEP = IRVAL(14026,0)
IRFN = IRVAL(14030,0)
IVI2 = IRVAL(13764,0)

```

```

C
C  THESE IRVAL FUNCTIONS READ THE MEMORY LOCATIONS
C  CORRESPONDING TO THESE PARAMETERS (ALL ARE INTEGERS):
C

```

(OCTAL)	LOCATION	PARAMETER
	13004	INODE NO.
	14000	NDP (=INTEGER/256)
	14001	FSZ (=INTEGER/512)
	14022	DFN
	14025	XSP
	14026	XEP

```

C *****
C
C  READ FTIR PARAMETERS FOR SETTING SUBROUTINE FLAGS:
C  (1=CTFE, 2= CH4, 3= H2O, 4= O3, 5= ??, 6= ??)
C

```

```

IFLAG1 = IRVAL(13710,0)
IFLAG2 = IRVAL(13713,0)
IFLAG3 = IRVAL(13714,0)
IFLAG4 = IRVAL(13715,0)

```

```

IFLAG5 = IRVAL(13731,0)
IFLAG6 = IRVAL(13750,0)
C
C
C THESE IRVAL FUNCTIONS READ THE MEMORY LOCATIONS
C CORRESPONDING
C TO THESE PARAMETERS (ALL ARE INTEGERS):
C
C      (OCTAL)      LOCATION      PARAMETER
C      13710              WTY
C      13713              SMN
C      13714              SIZ
C      13715              ITR
C      13731              MNT
C      13750              RTO
C
C *****
C
C THE FIRST 88 SECTORS OF THE SCRATCH AREA (I.E., SECTORS 0-
C 87) CONTAIN MISCELLANEOUS INFORMATION. SCRATCH FILE 0
C BEGINS AT SECTOR 88 AND OCCUPIES FSZ/512 SECTORS. ALL
C SUBSEQUENT FILES ARE THE SAME SIZE AS FILE 0.
C
C THE LAST SECTOR OF EACH FILE IS THE FILE STATUS BLOCK.THERE
C ARE A CONSIDERABLE NUMBER OF SECTORS BETWEEN THE END OF THE
C DATA AND THE BEGINNING OF THE FILE STATUS BLOCK. IT IS NOT
C CLEAR WHAT THESE EXTRA SECTORS ARE USED FOR.
C
C *****
C
C LOCATE SECTORS TO BE READ USING THE FOLLOWING INDEX.
C
C      IDFSEC=(IDFN+1)*NSECS+87
C      PRINT 998, IDFSEC
C 998      FORMAT(' ',IDFSEC= ',I6,/')
C
C *****
C
C READ HEADER BLOCK INFORMATION USING IRTISK. STORE RESULTS
C IN AN ARRAY CALLED IDATA.
C
C      CALL IRTISK(IDATA,512,IDFSEC,INODE)
C      DO 10 I=1,17
C          PRINT 1000, I,IDATA(I)
C1000      FORMAT(' ',IDATA',I2,2X,' = ',I6)
C 10      CONTINUE
C
C NOW, FILE STATUS INFO CAN BE DETERMINED FROM THE ELEMENTS
C OF IDATA:
C
C      IABS = ABSORBANCE FLAG, 0 IF ABSORBANCE
C      IPTS = NO. OF DATA POINTS
C      FEXP = EXPONENT FOR FILE SCALING
C      FXAX = DATA POINT SPACING ON X AXIS

```

```

C
  IABS = IDATA(10)
  IF (IABS.NE.0) GOTO 900
  IPTS = IDATA(15)*128
  FEXP = 2**(19-IDATA(6))
  FXAX = FLASER/(IPTS*IDATA(17))

C
C -----
C
C NOW DETERMINE THE STARTING AND ENDING POINTS FOR THE FILE
C TO BE READ. THIS IS DONE BY TWO SEQUENTIAL IF - ENDIF
C LOOPS.THE FIRST SETS ISTEP EQUAL TO THE LESSER OF XSP AND
C XEP (WHICH ARE READ FROM THE FT-IR SCRATCH FILE HEADER
C BLOCK). THE SECOND LOOP CONVERTS THE XSP AND XEP VALUES
C FROM CM-1 TO SCRATCH FILE DATA POINT VALUES. THE 0.5
C FACTOR WHICH IS ADDED ENSURES THAT INTEGER ISTEP AND IENP
C VALUES ARE ROUNDED CORRECTLY.
C
  IF (IXSP.LE.IXEP) THEN
    ISTEP = IXSP
    IENP = IXEP
  ELSE
    ISTEP = IXEP
    IENP = IXSP
  ENDIF
  IF (IXSP.GT.IXEP) THEN
    ISTEP = IXEP/FXAX+0.5
    IENP = IXSP/FXAX+0.5
  ELSE
    ISTEP = IXSP/FXAX+0.5
    IENP = IXEP/FXAX+0.5
  ENDIF
  NP = IENP-ISTEP+1
  PRINT 850, ISTEP,IENP,NP
C 850 FORMAT(' ',/, ' ISTEP= ',I6,2X, 'IENP= ',I6,2X, 'NP= '
&,I6,/)

C
C CHECK FOR A REASONABLE NO. OF PTS. IN NP
C
  IF (NP.GT.NPMAX) THEN
    WRITE(2,901) NPMAX,NP
  ELSEIF (NP.LT.5) THEN
    WRITE(2,902) NP
  ENDIF

C
C NOW READ DATA FROM SCRATCH FILE DFN INTO ARRAY IDA
C
C IN IS A COUNTER. NDONE TAKES THE DATA POINT VALUE OF ISTEP
C AND CONVERTS IT TO SECTORS. NSKIP TAKES THE STARTING DATA
C POINT VALUE (ISTEP) AND SUBTRACTS AN INTEGER NO. OF DATA
C POINTS, BY SECTOR, FROM IT, LEAVING THE POINT IN THE
C SELECTED SECTOR WHERE DATA REPRESENTING THE INTERVAL ISTEP -
C IENP BEGIN.
C

```

```

      IN = 1
      NDONE = ISTD/512
      NSKIP = ISTD-NDONE*512
C      PRINT 400, NDONE, NSKIP
C 400  FORMAT(' ',/, ' NDONE= ',I8,2X, 'NSKIP= ',I8,/)
C
C IF THE SCRATCH FT-IR FILE HAD XSP=0 OR XEP=0, THEN DATA CAN
C BE READ DIRECTLY, ONCE THE PROPER BEGINNING SECTOR IS
C SPECIFIED. IF XSP OR XEP WERE NOT ZERO, THEN NDONE SECTORS
C PLUS NSKIP POINTS MUST BE SKIPPED OVER TO BEGIN READING
C DATA.
C
C
C RESET FLAG FOR BASELINE CORRECTION ROUTINE
C
      IFLAG=0
      IF (NSKIP.GT.0) THEN
C
C SET FLAG FOR BASELINE CORRECTION ROUTINE
C
      IFLAG=1
      CALL IRTISK(IDA,512,88+IDFN*NSECS+NDONE,INODE)
      DO 20 I=NSKIP+1,512
        IDA(IN) = IDA(I)
        IN = IN + 1
20    CONTINUE
      NDONE = NDONE + 1
      ENDIF
C
C NPREM IS A COUNTER WHICH TELLS HOW MANY DATA POINTS TO READ
C FROM THE FT-IR SCRATCH FILE TO COVER THE INTERVAL SPECIFIED
C BY ISTD AND IENP.
C
      NPREM = NP-IN+1
C      PRINT 402, IN,NPREM
C 402  FORMAT(' ', 'IN= ',I6,2X, 'NPREM= ',I10,/)
      IF (NPREM.GT.0) THEN
        CALL
        IRTISK(IDA(IN),NPREM,88+IDFN*NSECS+NDONE,INODE)
      ENDIF
C
C NOW THE POINTS IN THE INTEGER ARRAY IDA ARE CONVERTED TO
C REAL VALUES BY DIVIDING EACH ONE BY FEXP (SEE FT-IR
C SOFTWARE MANUAL, P. 18-5 FOR AN EXPLANATION). NOTE THAT
C ANY TOTALLY ABSORBING DATA POINTS HAVE THE VALUE -524288
C AND THESE ARE SET EQUAL TO ZERO IN THE REAL DATA ARRAY.
C
      DO 50 I = 1,NP
        IDAS = IDA(I)
        IF (IDAS.EQ.-524288) IDAS = 0
        Y(I) = IDAS/FEXP
C      PRINT 403,I,Y(I)
C403  FORMAT(' ', 'X(',I3,')=' ,F6.3)
      50  CONTINUE

```

```

C      DO 51 I=1980,2032
C          WN=(I-1)*FXAX
C          PRINT 71,WN,Y(I)
C 71      FORMAT(' ', 'WN=',F8.3,2X, 'Y=',F8.3)
C 51      CONTINUE
C
C *****
C NOW THAT THE DATA POINTS ARE AVAILABLE, BASELINE CORRECTION
C CAN BE MADE. THE CORRECTION WILL BE MADE IN THE SAME
C MANNER IT WOULD BE DONE BY HAND. A POINT ON ONE SIDE OF
C THE ANALYTICAL PEAK WILL BE CHOSEN BY AVERAGING THE
C ABSORBANCE VALUES OVER A CERTAIN PORTION OF THE X-AXIS.
C FOR SPECIES WHICH HAVE HIGHLY STRUCTURED PEAKS, THIS MAY BE
C A VERY SHORT DISTANCE (E.G., METHANE USES A 2 CM-1 ONE ONE
C SIDE OF THE ANALYTICAL PEAK AND A 1.0 CM-1 INTERVAL ON THE
C OTHER. THESE INTERVALS ARE BASED ON EXPANDED PLOTS AND ARE
C CHOSEN TO GIVE POINTS CLOSE TO THOSE ONE WOULD CHOOSE IF
C DOING THE BASELINE CORRECTION BY HAND). THE SAME THING IS
C DONE ON THE OTHER SIDE OF THE ANALYTICAL PEAK. THESE
C POINTS WILL BE DEFINED WITHIN THE SUBROUTINE FOR EACH
C SEPARATE SPECIES.
C *****
C
C
C TO CONFORM WITH LOTUS 1-2-3 DATE FORMAT, READ THE VALUE OF
C RTP, THEN PRINT THIS AS LDATE
C
C      LDATE = IRVAL(13751,0)
C
C TO AVOID EXTRA CHARACTERS IN THE TIME PRINTOUT,
C PICK OUT THE CHARACTERS NEEDED FROM THE IDATA ARRAY AND
C CONCATENATE THEM INTO THE NECESSARY OUTPUT.
C
C      DO 25 I=58,65
C          IF (I.EQ.58) THEN
C              H1=CHAR(IDATA(I))
C          ELSEIF (I.EQ.59) THEN
C              H2=CHAR(IDATA(I))
C          ELSEIF (I.EQ.61) THEN
C              N1=CHAR(IDATA(I))
C          ELSEIF (I.EQ.62) THEN
C              N2=CHAR(IDATA(I))
C          ELSEIF (I.EQ.64) THEN
C              S1=CHAR(IDATA(I))
C          ELSE (I.EQ.65)
C              S2=CHAR(IDATA(I))
C          ENDIF
C 25      CONTINUE
C
C CONCATENATE THE APPROPRIATE IDATA ELEMENTS TO FORM TIME
C CHARACTERS WHICH CAN BE PRINTED.
C
C          HH = H1 // H2
C          NN = N1 // N2

```



```

      SS = S1 // S2
C
C RETRIEVE THE TEMPERATURE CHARACTERS FROM THE IDATA ARRAY
C (THESE CHARACTERS ARE WRITTEN TO THE IDATA ARRAY DURING
C DATA
C ACQUISITION UNDER THE MACRO DA5 WITH THE FORTRAN PROGRAM
C "OTEMP.FTN")
C
      CT1=CHAR(IDATA(68))
      CT2=CHAR(IDATA(69))
      CT3=CHAR(IDATA(70))
      CT4=CHAR(IDATA(71))
C
C NOW, CONCATENATE THESE CHARACTERS TO FORM THE TEMPERATURE
C
      CTEMP=CT1 // CT2 // CT3 // CT4
C
C DETERMINE WHICH SPECIES ARE TO BE ANALYZED.
C
      844 IF (IFLAG1.EQ.1) CALL CTFE(Y,FXAX,CABS)
           A1=CABS
C      PRINT*, 'COMPUTED A1'
           IF (IFLAG2.EQ.1) CALL CH4(Y,FXAX,CABS)
           A2=CABS
C      PRINT*, 'COMPUTED A2'
           IF (IFLAG3.EQ.1) CALL H2O(Y,FXAX,CABS)
           A3=CABS
C      PRINT*, 'COMPUTED A3'
           IF (IFLAG4.EQ.1) CALL O3(Y,FXAX,CABS)
           A4=CABS
C      PRINT*, 'COMPUTED A4'
           IF (IFLAG5.EQ.1) CALL ?? (Y,FXAX,CABS)
           A5=CABS
C      IF (IFLAG6.EQ.1) CALL ?? (Y,FXAX,CABS)
           A6=CABS
C
      PRINT 155, LDATE, HH, NN, SS, CTEMP, A1, A2, A3, A4
C      PRINT*, 'COMPLETED PRINT TO SCREEN!!'
      OPEN(11, FILE='HOLD.DAT', STATUS='OLD')
      WRITE(11,150) LDATE, HH, NN, SS, CTEMP, A1, A2, A3, A4
C      PRINT*, 'COMPLETED WRITE TO HOLD.DAT!!'
C
      150 FORMAT(I5,2X,3(A2,2X),A4,2X,F6.3,2X,F6.3,2X,F6.3,
           & 2X,F6.3)
      155 FORMAT(1X,I5,2X,3(A2,2X),A4,4(2X,F6.3))
C
      CLOSE(11)
C
      GOTO 999
C
C FORMAT STATEMENTS
C
      900 WRITE(2,990) IDATA(10)
      901 FORMAT(' ',/, ' ONLY DIMENSIONED TO ',I6, ' PTS', ' NOT '

```

```

      &,I6,,)
    902 FORMAT(' ','WHY ARE THERE ONLY ',I6,' PTS.
REQUESTED?',/,)
    990 FORMAT(' ',/,/, ' ABSORBANCE FLAG = ',I2,2X,'NOT AN '
      &,'ABSORBANCE FILE',/)
    999  CONTINUE
          CALL EXIT
          END

```

BATCH FILE USED TO COMPILE THE ABOVE PROGRAM.

NAME: EXP4.BAT

LISTING

```

RUN FORTRAN
EXP4.ASC:L
RUN FORTRAN
CTFE.ASC:L
RUN FORTRAN
CH4.ASC:L
RUN FORTRAN
NH3.ASC:L
RUN FORTRAN
H2O.ASC:L
RUN RELOAD
:B=1000-53777
EXP4.REL:L
CTFE.REL:L
CH4.REL:L
NH3.REL:L
H2O.REL:L
IRVAL.REL [ROOT,HLIB]:L
FORRUN.LIB [ROOT,HLIB]:R
NICAPL.LIB [ROOT,HLIB]:R
DPSYS.LIB [ROOT,HLIB]:R
FIOS.LIB [ROOT,HLIB]:R
NICSYS.LIB [ROOT,HLIB]:R
/-TT:U
/EXP4.FTN:S
DEL EXP4.REL
DEL EXP4.TMP
DEL CTFE.REL
DEL CTFE.TMP
DEL CH4.REL
DEL CH4.TMP
DEL NH3.REL
DEL NH3.TMP
DEL H2O.REL
DEL H2O.TMP

```

APPENDIX F

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO STORE DATA IN AN ASCII FILE ON THE NICOLET FOR LATER ANALYSIS AND PLOTTING

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   APP4.ASC   (stores absorbance values for 4 species)
C
C   THIS PROGRAM WAS DESIGNED TO READ THE OUTPUT FILE
C   FROM THE PROGRAM EXP4.FTN.  THE NAME OF THE EXP4.FTN
C   OUTPUT FILE IS HOLD.DAT.  IT CONTAINS A SINGLE LINE
C   OF DATA WHICH CONSISTS OF DATE, TIME, TEMPERATURE,
C   AND ABSORBANCE VALUES FOR 4 SPECIES
C
C   THIS PROGRAM THEN READS THE PREEXISTING DATA FILE
C   IROUT.DAT.  THIS FILE CONTAINS ALL OF THE PREVIOUS
C   DATA WRITTEN TO THE FILE HOLD.DAT.  ONCE ALL OF THE
C   DATA IS READ, THE FILE IS THEN OVERWRITTEN WITH THE
C   ADDITION OF THE SINGLE LINE OF DATA JUST READ FROM
C   HOLD.DAT.  THE RESULT IS A ROUND ABOUT WAY OF
C   APPENDING DATA TO A FILE.
C
C   AT THE TOP OF THE FILE IROUT.DAT IS A HEADER WHICH
C   CONSISTS OF THE NUMBER OF ENTRIES THUS FAR IN THE
C   FILE IROUT.DAT.  WHEN STARTING A RUN, THIS FILE MUST
C   CONTAIN AT LEAST A SINGLE LINE OF DUMMY VALUES IN
C   THE PROPER FORMAT.
C
C   A MAXIMUM OF 400 SAMPLES CAN BE HANDLED BY THIS
C   PROGRAM.
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

```

      INTEGER  HH,NN,SS
      REAL  CTEMP
      INTEGER  HUMID
      REAL  A1,A2,A3,A4
      INTEGER  I, M, NUMP, MAXPOINTS, LDATE
      PARAMETER (MAXPOINTS=400)
      PARAMETER (M=5)
      REAL  RDAT1 (MAXPOINTS), RDAT2 (MAXPOINTS)
      REAL  RDAT3 (MAXPOINTS), RDAT4 (MAXPOINTS)
      INTEGER  CHARDAT (MAXPOINTS, M)
      INTEGER  LDATEVECT (MAXPOINTS)
      REAL  CTEMPVECT (MAXPOINTS)
C
C GET THE NEW CALCULATED DATA FROM DISK

```

```

C
C      PRINT*, 'APP.FTN --- BEFORE HOLD.DAT OPENED'
      OPEN(11, FILE='HOLD.DAT', STATUS='OLD')
      READ(11, 155) LDATE, HH, NN, SS, CTEMP, A1, A2, A3, A4
      CLOSE(11)
C
C OPEN AND READ FILE OF PAST VALUES
C
C      PRINT*, 'APP.FTN -- BEFORE IROUT.DAT OPEN'
      OPEN(11, FILE='IROUT.DAT', STATUS='OLD')
      READ(11, 140) NUMP
C      PRINT*, 'APP.FTN -- VALUE FOR NUMP= ', NUMP
      IF (NUMP.GT.0) THEN
        DO 860, I = 1, NUMP
          READ(11, 155) LDATEVECT(I), CHARDAT(I,1),
            &CHARDAT(I,2), CHARDAT(I,3), CTEMPVECT(I), RDAT1(I),
            &RDAT2(I), RDAT3(I), RDAT4(I)
860    CONTINUE
        ENDIF
        CLOSE(11)
C
C REOPEN THE SAME FILE AND WRITE DATA + NEW DATA
C
      NUMP = NUMP+1
      OPEN(11, FILE='IROUT.DAT', STATUS='OLD')
      WRITE(11, 140) NUMP
      IF (NUMP.GT.1) THEN
        DO 870, I = 1, NUMP-1
          WRITE(11, 155) LDATEVECT(I), CHARDAT(I, 1),
            &CHARDAT(I,2), CHARDAT(I,3), CTEMPVECT(I), RDAT1(I),
            &RDAT2(I), RDAT3(I), RDAT4(I)
870    CONTINUE
        ENDIF
        WRITE(11,155) LDATE, HH, NN, SS, CTEMP, A1, A2, A3, A4
140    FORMAT(I5)

155    FORMAT(I5,2X,3(I2,2X),F4.1,2X,4(F6.3,2X))

      CLOSE(11)
      CALL EXIT
      END

```

APPENDIX G

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO CALCULATE THE BASELINE-CORRECTED ABSORBANCE VALUE FOR CTFE VAPOR AT 1205 CM-1

C*****C

```

      SUBROUTINE CTFE(Y,FXAX,CABS)
      REAL  Y(22528),BP1,BP2,PXA,PYA,CABS,XDIF,XDIF2,YDIF,
1FAC1,FAC2,EP,SP,IC
      INTEGER COUNT
C
C TAKES THE SET BASELINE POINTS AND CALCULATES A BASELINE-
C CORRECTED ABSORBANCE VALUE FOR THE ANALYTICAL PEAK AT
C 1205 CM-1. THEN PRINTS OUT THE VALUE.
C
C
C DEFINE THE BASELINE POINTS FOR THE CTFE ANALYTICAL PEAK
C
      IPT1=1309/FXAX
      IPT2=1311/FXAX
      IPT3=1080/FXAX
      IPT4=1085/FXAX
C
C      PRINT 35, IPT1,IPT2,IPT3,IPT4
C 35      FORMAT(' ', 'IPT1=', I4, 2X, 'IPT2=', I4, 2X, 'IPT3=', I4, 2X,
C      1 'IPT4=', I4, /) C
C AVERAGE THE POINTS FOR THE 1ST BASELINE VALUE
C
      SP = 0
      BP1= 0
      COUNT = 0
      IFIRST=IPT1
      ILAST =IPT2
C
C NOW CALCULATE FIRST BASELINE POINT
C
C      PRINT 36, IFIRST,ILAST
C 36      FORMAT(' ', 'IFIRST=', I4, 2X, 'ILAST=', I4, /)
      DO 70 I=IFIRST,ILAST
      SP=SP+Y(I)
      COUNT=COUNT+1
C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
      WN=(I-1)*FXAX
      PRINT 37,WN,Y(I),SP,COUNT
C 37      FORMAT(' ', 'WN=', F8.3, 2X, 'Y(I)=', F8.3, 2X,
C      &'SP=', F8.3,
C      12X, 'COUNT=', I6)
C 70      CONTINUE

```

```

      BP1=SP/COUNT
C
C AVERAGE THE POINTS FOR THE 2ND BASELINE VALUE
C
      EP = 0
      BP2 = 0
      COUNT = 0
      ISTART=IPT3
      IEND =IPT4
C
C NOW CALCULATE THE SECOND BASELINE POINT
C
C      PRINT 39, ISTART,IEND
C 39      FORMAT(' ', 'ISTART=', I4, 2X, 'IEND =', I4, /)
      DO 80 I=ISTART,IEND
          EP=EP+Y(I)
          COUNT=COUNT+1
C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
      WN=(I-1)*FXAX
      PRINT 38, WN, Y(I), SP, COUNT
C 38      FORMAT(' ', 'WN=', F8.3, 2X, 'Y(I)=', F8.3,
C          2X, 'SP=', F8.3,
C          12X, 'COUNT=', I6)
      80      CONTINUE
      BP2=EP/COUNT
C
C PRINT OUT THE BASELINE DETERMINING POINTS
C
C      PRINT 85, BP1, BP2
C 85      FORMAT(' ', 'BP1= ', F9.4, 2X, 'BP2= ', F9.4, /)
C
C DETERMINE THE X,Y VALUES (CM-1 AND ABS.) FOR THE
C ANALYTICAL PEAK (1205 CM-1) BY FINDING THE MAXIMUM Y VALUE
C IN THE INTERVAL FOR THIS PEAK WHICH IS: 1207 CM-1 TO 1203
C CM-1 (OR IN DATA POINT VALUES: 2503 TO 2495).
C
      PXA=0
      PYA=0
      DO 82 I=2495,2503
          IF (Y(I).GT.Y(I-1)) THEN
              PYA=Y(I)
              IC=I-1
              PXA=IC*FXAX
          ENDIF
C          PRINT 299, I, Y(I), PYA, IC, PXA
C 299      FORMAT(' ', 'I=', I4, 2X, 'Y=', F8.3, 2X, 'PYA=', F8.3, 2X,
C          1 'IC=', F8.3, 2X, 'PXA=', F8.3)
      82      CONTINUE
C      PRINT 86, PXA, PYA
C 86      FORMAT(' ', 'PXA= ', F8.3, 2X, 'PYA= ', F8.3, /)
C
C CALCULATE THE BASELINE CORRECTION. THERE ARE TWO POSSIBLE

```

```

C CASES: (A) POSITIVE SLOPING BASELINE, OR (B) NEGATIVE
C SLOPING BASELINE.
C
C          CASE (A) - POSITIVE SLOPING BASELINE (BP1 < BP2)
C
C SKIP TO CASE (B) IF BASELINE SLOPE IS NEGATIVE
C
C          IF(BP1.GT.BP2) GOTO 3000
C
C OTHERWISE PROCEED WITH THE CORRECTION
C
C          DP1=(1309+1309)/2
C          DP2=(1085+1080)/2
C          YDIF=BP2-BP1
C          XDIF=DP1-DP2
C          XDIF2=DP1-PXA
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+BP1
C          PRINT 87, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 87      FORMAT(' ', 'DP1=',F8.3,2X,'DP2=',F8.3,
C          2X,'YDIF=',F9.4,2X,
C          &'XDIF=',F9.4,2X,'XDIF2=',F9.4,2X,/, 'FAC1=',
C          &F9.4,2X,'FAC2=',F9.4,/)
C          GOTO 3500
C
C          CASE (B) - NEGATIVE SLOPING BASELINE (BP1 > BP2)
C
C 3000      CONTINUE
C          DP1=(1309+1311)/2
C          DP2=(1085+1080)/2
C          YDIF=BP1-BP2
C          XDIF=DP1-DP2
C          XDIF2=PX1-DP2
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+BP2
C 3500      CONTINUE
C
C APPLY THE CORRECTION TO THE ABSORBANCE VALUE FROM PPK
C
C          CABS=PYA-FAC2
C
C PRINT OUT CORRECTED ABSORBANCE VALUE
C
C          PRINT 88, CABS
C 88      FORMAT(' ', 'CTFE= ',F4.3)
C          PRINT*, ' '
C END THE SUBROUTINE
C          RETURN
C          END

```

[NOTE: this subroutine is compiled as a part of the EXP4 batch file. See APPENDIX E for the listing]

APPENDIX H

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO CALCULATE THE BASELINE-CORRECTED ABSORBANCE VALUES FOR METHANE VAPOR AT 1305 CM-1

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      SUBROUTINE CH4(Y,FXAX,CABS)
C
C      CALCULATES THE BASELINE BY TAKING THE AVERAGE OF POINTS
C      ON ONE SIDE OF THE ANALYTICAL PEAK (3026 - 3023 CM-1)
C      FOR THE BEGINNING POINT. THEN TAKING THE AVERAGE OF
C      POINTS ON THE OTHER SIDE OF THE ANALYTICAL PEAK (2996 -
C      2992) FOR THE ENDING POINT. A LINE CONNNECTING THESE
C      TWO POINTS FORMS THE BASELINE. THE ABSORBANCE VALUE AT
C      THE FIRST ANALYTICAL PEAK (3018 CM-1) IS THEN CORRECTED
C      TO THIS MEASURED BASELINE. THE SECOND ANALYTICAL PEAK
C      AT 1305 CM-1 IS CORRECTED SIMILARLY. (ONLY THE 1305
C      CM-1 PEAK WAS USED IN THIS STUDY.)
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      SUBROUTINE CH4(X,FXAX)
C      REAL X(22528),BP1,LBP,PXA,PYA,CABS,XDIF,XDIF2,YDIF,
C      1FAC1,FAC2,EP,SP,IC
C      INTEGER COUNT
C
C      DEFINE THE BASELINE POINTS FOR THE METHANE BAND AT 1305 CM-1
C
C      IPT1=1310/FXAX
C      IPT2=1308/FXAX
C      IPT3=1280/FXAX
C      IPT4=1279/FXAX
C
C      PRINT 35, IPT1,IPT2,IPT3,IPT4
C 35      FORMAT(' ','IPT1=',I4,2X,'IPT2=',I4,2X,'IPT3=',I4,2X,
C      1'IPT4=',I4,/)
C
C      AVERAGE THE POINTS FOR THE FIRST BASELINE VALUE
C
C      SP = 0
C      BP1= 0
C      COUNT = 0
C      IFIRST=IPT1
C      ILAST =IPT2
C
C      NOW CALCULATE FIRST BASELINE POINT
C
C      PRINT 38, IFIRST,ILAST
C 38      FORMAT(' ','IFIRST=',I4,2X,'ILAST=',I4,/)
C      DO 72 I=ILAST,IFIRST

```



```

        SP=SP+X(I)
        COUNT=COUNT+1
C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C        WN=(I-1)*FXAX
C        PRINT 39,WN,X(I),SP,COUNT
C 39      FORMAT(' ', 'WN=', F8.3, 2X, 'X(I)=', F8.3, 2X,
C        &'SP=', F8.3, 2X,
C        1'COUNT=', I6)
C 72      CONTINUE
C        BP1=SP/COUNT
C
C AVERAGE THE POINTS FOR THE 2ND BASELINE VALUE
C
C        EP = 0
C        LBP = 0
C        COUNT = 0
C        IFIRST=IPT3
C        ILAST =IPT4
C
C NOW CALCULATE THE SECOND BASELINE POINT
C
C        DO 83 I=ILAST,IFIRST
C            EP=EP+X(I)
C            COUNT=COUNT+1
C 83      CONTINUE
C        LBP=EP/COUNT
C
C PRINT OUT THE BASELINE DETERMINING POINTS
C
C        PRINT 67, BP1,LBP
C 67      FORMAT(' ', 'BP1= ', F9.4, 2X, 'LBP= ', F9.4, /)
C
C DETERMINE THE X,Y VALUES (CM-1 AND ABS.) FOR THE
C ANALYTICAL PEAK (1305 CM-1) BY FINDING THE MAXIMUM Y VALUE
C IN THE INTERVAL FOR THIS PEAK WHICH IS: 1307 CM-1 TO 1304
C CM-1 (OR IN DATA POINT VALUES: 2710 TO 2704).
C
C        PXA=0
C        PYA=0
C        DO 84 I=2704,2710
C            IF (X(I).GT.X(I-1)) THEN
C                PYA=X(I)
C                IC=I-1
C                PXA=IC*FXAX
C            ENDIF
C        PRINT 399,I,X(I),PYA,IC,PXA
C 399      FORMAT(' ', 'I=', I4, 2X, 'X=', F8.3, 2X, 'PYA=', F8.3, 2X,
C        1'IC=', F8.3, 2X, 'PXA=', F8.3)
C 84      CONTINUE
C        PRINT 89,PXA,PYA
C 89      FORMAT(' ', 'PXA= ', F8.3, 2X, 'PYA= ', F8.3, /)
C

```

```

C CALCULATE THE BASELINE CORRECTION.  THERE ARE TWO POSSIBLE
C CASES:  (A) POSITIVE SLOPING BASELINE, OR (B) NEGATIVE
C SLOPING BASELINE.
C
C          CASE (A) - POSITIVE SLOPING BASELINE (BP1 < LBP)
C
C SKIP TO CASE (B) IF BASELINE SLOPE IS NEGATIVE
C
C          IF(BP1.GT.LBP) GOTO 3100
C
C OTHERWISE PROCEED WITH THE CORRECTION
C
C          DP1=(1310+1308)/2
C          DP2=(1280+1279)/2
C          YDIF=LBP-BP1
C          XDIF=DP1-DP2
C          XDIF2=DP1-PXA
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+BP1
C          PRINT 187, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 187      FORMAT(' ', 'DP1=', F8.3, 2X, 'DP2=', F8.3, 2X,
C          &'YDIF=', F9.4, 2X,
C          &'XDIF=', F9.4, 2X, 'XDIF2=', F9.4, 2X, /, 'FAC1=',
C          &F9.4, 2X, 'FAC2=', F9.4, /)
C          GOTO 4500
C
C          CASE (B) - NEGATIVE SLOPING BASELINE (BP1 > LBP)
C
C 3100      CONTINUE
C          DP1=(1310+1308)/2
C          DP2=(1280+1279)/2
C          YDIF=BP1-LBP
C          XDIF=DP1-DP2
C          XDIF2=PX1-DP2
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+LBP
C 4500      CONTINUE
C APPLY THE CORRECTION TO THE ABSORBANCE VALUE FROM PPK
C
C          CABS=PYA-FAC2
C
C PRINT OUT CORRECTED ABSORBANCE VALUE
C          PRINT 188, CABS
C 188      FORMAT(' ', 'PEAK ABS(CH4,1305 CM-1)= ', F6.3, /, 35(' - '),
C          &1/)
C END THE SUBROUTINE
C
C          RETURN
C          END

```

[NOTE: this program is compiled and linked as a subroutine of EXP4. See Appendix E for the applicable batch file listing.]

APPENDIX I

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO CALCULATE THE BASELINE-CORRECTED ABSORBANCE VALUE FOR WATER VAPOR AT 1700 CM-1

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C      SUBROUTINE H2O(Y,FXAX,CABS)                                C
C                                                                 C
C      CALCULATES THE BASELINE BY TAKING THE AVERAGE OF POINTS C
C      ON ONE SIDE OF THE ANALYTICAL PEAK (1703 - 1702 CM-1) C
C      FOR THE BEGINNING POINT. THEN TAKING THE AVERAGE OF C
C      POINTS ON THE OTHER SIDE OF THE ANALYTICAL PEAK (1694 - C
C      1691 CM-1) FOR THE ENDING POINT. A LINE CONNNECTING C
C      THESE TWO POINTS FORMS THE BASELINE. THE ABSORBANCE C
C      VALUE AT THE ANALYTICAL PEAK (1700 CM-1) IS THEN C
C      CORRECTED TO THIS MEASURED BASELINE. C
C                                                                 C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      SUBROUTINE H2O(Y,FXAX,CABS)
C
C      REAL  Y(22528),BP1,LBP,FXA,PYA,CABS,XDIF,XDIF2,YDIF,
1FAC1,FAC2,EP,SP,IC
C      INTEGER COUNT
C
C      DEFINE THE BASELINE POINTS FOR THE WATER ANALYTICAL PEAK
C
C      IPT1=1703/FXAX
C      IPT2=1702/FXAX
C      IPT3=1694/FXAX
C      IPT4=1691/FXAX
C
C      PRINT 35, IPT1,IPT2,IPT3,IPT4
C 35  FORMAT(' ', 'IPT1=', I4, 2X, 'IPT2=', I4, 2X, 'IPT3=', I4, 2X,
C      1 'IPT4=', I4, /)
C
C      AVERAGE THE POINTS FOR THE 1ST BASELINE VALUE
C
C      SP = 0
C      BP1= 0
C      COUNT = 0
C      IFIRST=IPT1+1
C      ILAST =IPT2
C
C      NOW CALCULATE FIRST BASELINE POINT
C
C      PRINT 36, IFIRST,ILAST
C 36  FORMAT(' ', 'IFIRST=', I4, 2X, 'ILAST=', I4, /)
C      DO 70 I=ILAST,IFIRST
C          SP=SP+Y(I+1)
C          COUNT=COUNT+1

```

```

C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C          WN=(I)*FXAX
C          PRINT 37, WN,Y(I+1),SP,COUNT
C 37      FORMAT(' ', 'WN=', F8.3, 2X, 'Y(I)=', F8.3,
C          &2X, 'SP=', F8.3,
C          12X, 'COUNT=', I6)
C 70      CONTINUE
C          BP1=SP/COUNT
C
C AVERAGE THE POINTS FOR THE 2ND BASELINE VALUE
C
C          EP = 0
C          LBP = 0
C          COUNT = 0
C          IFIRST=IPT3+1
C          ILAST =IPT4
C
C NOW CALCULATE THE SECOND BASELINE POINT
C
C          DO 80 I=ILAST,IFIRST
C              EP=EP+Y(I+1)
C              COUNT=COUNT+1
C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C          WN=(I)*FXAX
C          PRINT 140
C 140      FORMAT(' ')
C          PRINT 137, WN,Y(I+1),SP,COUNT
C 137      FORMAT(' ', 'WN=', F8.3, 2X, 'Y(I)=', F8.3,
C          &2X, 'SP=', F8.3,
C          12X, 'COUNT=', I6)
C 80      CONTINUE
C          LBP=EP/COUNT
C
C PRINT OUT THE BASELINE DETERMINING POINTS
C
C          PRINT 85, BP1,LBP
C 85      FORMAT(' ', 'BP1= ', F9.4, 2X, 'LBP= ', F9.4,/)
C
C DETERMINE THE X,Y VALUES (CM-1 AND ABS.) FOR THE
C ANALYTICAL PEAK (1700 CM-1) BY FINDING THE MAXIMUM Y VALUE
C IN THE INTERVAL FOR THIS PEAK WHICH IS: 1702 CM-1 TO 1699
C CM-1 (OR IN DATA POINT VALUES: 3530 TO 3523).
C
C          PXA=0
C          PYA=0
C          DO 82 I=3523,3530
C              IF (Y(I).GT.Y(I-1)) THEN
C                  PYA=Y(I)
C                  IC=I-1
C                  PXA=IC*FXAX

```

```

        ENDIF
C          PRINT 299,I,Y(I),PYA,IC,PXA
C299      FORMAT(' ','I=',I4,2X,'Y=',F8.3,2X,'PYA=',F8.3,2X,
C          1'IC=',F8.3,2X,'PXA=',F8.3)
C          82 CONTINUE
C          PRINT 86,PXA,PYA
C 86      FORMAT(' ','PXA= ',F8.3,2X,'PYA= ',F8.3,/)
C
C CALCULATE THE BASELINE CORRECTION. THERE ARE TWO POSSIBLE
C CASES: (A) POSITIVE SLOPING BASELINE, OR (B) NEGATIVE
C SLOPING BASELINE.
C
C          CASE (A) - POSITIVE SLOPING BASELINE (BP1 < LBP)
C
C SKIP TO CASE (B) IF BASELINE SLOPE IS NEGATIVE
C
C          IF(BP1.GT.LBP) GOTO 3000
C
C OTHERWISE PROCEED WITH THE CORRECTION
C
C          DP1=(1703+1702)/2
C          DP2=(1694+1691)/2
C          YDIF=LBP-BP1
C          XDIF=DP1-DP2
C          XDIF2=DP1-PXA
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+BP1
C          PRINT 87, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 87      FORMAT(' ','DP1=',F8.3,2X,'DP2=',F8.3,
C          &2X,'YDIF=',F9.4,2X,
C          &'XDIF=',F9.4,2X,'XDIF2=',F9.4,2X,/, 'FAC1=',
C          &F9.4,2X,'FAC2=',F9.4,/)
C          GOTO 3500
C
C          CASE (B) - NEGATIVE SLOPING BASELINE (BP1 > LBP)
C
C 3000 CONTINUE
C          DP1=(1703+1702)/2
C          DP2=(1694+1691)/2
C          YDIF=BP1-LBP
C          XDIF=DP1-DP2
C          XDIF2=PXA-DP2
C          FAC1=XDIF2/XDIF
C          FAC2=FAC1*YDIF
C          FAC2=FAC2+LBP
C          PRINT 57, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 57      FORMAT(' ','DP1=',F8.3,2X,'DP2=',F8.3,
C          &2X,'YDIF=',F9.4,2X,
C          &'XDIF=',F9.4,2X,'XDIF2=',F9.4,2X,/, 'FAC1=',
C          &F9.4,2X,'FAC2=',F9.4,/)
C 3500 CONTINUE
C
C APPLY THE CORRECTION TO THE ABSORBANCE VALUE FROM PPK

```

```
C
      CABS=PYA-FAC2
C
C PRINT OUT CORRECTED ABSORBANCE VALUE
C
C      PRINT 88, CABS
C 88      FORMAT(' ', 'CABS=', F4.3, '/')
C END THE SUBROUTINE
      RETURN
      END
```

[NOTE: this program was compiled and linked as a subroutine of EXP4.. See Appendix E for the applicable batch file listing.]

APPENDIX J

SOFTWARE LISTING FOR THE FORTRAN PROGRAM USED TO CALCULATE THE BASELINE-CORRECTED ABSORBANCE VALUE FOR OZONE AT 1055 CM-1

```

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   TAKES THE SET BASELINE POINTS AND CALCULATES A BASELINE- C
C   CORRECTED ABSORBANCE VALUE FOR THE O3 ANALYTICAL PEAK AT C
C   1055 CM-1 THEN PRINTS OUT THE VALUE. C
C
C   THIS VERSION OF THE SUBROUTINE HAS BEEN SPECIFICALLY C
C   DESIGNED TO MEASURE OZONE IN THE PRESENCE OF CTFE. THE C
C   INTERFERING CTFE ABSORBANCE IS FIRST MEASURED AND THEN C
C   SCALED AND SUBTRACTED OUT. THIS PROCESS IS DESCRIBED C
C   BELOW. DETERMINE THE SCALE FACTOR FOR SUBTRACTING C
C   OUT CTFE IN THE FOLLOWING WAY: C
C   (1) SELECT A REGION OF THE CTFE SPECTRUM WHICH DOES NOT C
C   OVERLAP ANY OZONE ABSORPTION AND FIND THE CTFE C
C   ABSORPTION MAXIMUM IN THAT REGION BY THE USUAL C
C   BASELINE CORRECTION TECHNIQUE. (THE BAND SELECTED IS C
C   THE ONE WHICH EXTENDS FROM 1111 TO 1148 CM-1 WITH C
C   A MAXIMUM AT 1130.578 CM-1.) C
C   (2) SUBTRACT OUT THE CTFE CONTRIBUTION FROM THE OZONE C
C   SPECTRUM IN THE 1037 - 1074 CM-1 REGION BY SCALING THE C
C   MEASURED CTFE ABSORBANCE WITH THE ABSORBANCE STORED IN C
C   THE DATA STATEMENTS THEN SUBTRACTING OUT THE CTFE C
C   CONTRIBUTION TO THE ABSORBANCE IN THE REGION OF INTEREST C
C   ON A POINT-BY-POINT BASIS. C
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

```

SUBROUTINE O3 (Y,FXAX,CABS)

```

      REAL Y(22528),BP1,BP2,PGA,PYA,CABS,XDIF,XDIF2,YDIF,
      1FAC1,FAC2,EP,SP,REF(100),SCALE,TEM,FXM,PYM,MAX
      INTEGER COUNT
      DATA REF/.128,.130,.132,.133,.136,.140,.144,.148,.151,
      1.156,.162,.167,.171,.175,.180,.184,.187,.190,.192,.195,
      2.196,.197,.197,.197,.196,.194,.192,.189,.187,.185,.180,
      3.176,.172,.168,.163,.158,.152,.148,.145,.141,.137,.134,
      4.132,.129,.127,.124,.123,.122,.120,.118,.116,.114,.111,
      5.108,.105,.101,.099,.096,.092,.088,.085,.083,.080,.078,
      6.076,.075,.074,.073,.073,.073,.073,.073,.073,.072,.073,
      7.073,.073,.074,.074/
C
      PGA=0
      PYA=0 I1=1124/FXAX I2=1134/FXAX MAX=0
C      PRINT*, ' '
C      PRINT*, '***** FIND THE CTFE PEAK ABS. AT 1130 CM-1C
C      PRINT*, ' '

```

```

DO 820 I=I1,I2
  IF (ABS(Y(I)).GT.MAX) THEN
    MAX=Y(I) PYA=MAX
    IC=I-1 PXA=IC*FXAX
C    PRINT 399,I,Y(I),PYA,PXA
C399    FORMAT(' ','I=',I4,2X,'Y=',F8.3,2X,\
C      &'PYA=',F8.3,2X,
C    1'PXA=',F8.3)
    ENDIF
  820 CONTINUE
C    PRINT 860,PXA,PYA
C860    FORMAT(' ','PXA= ',F8.3,2X,'PYA= ',F8.3,/)

C    NOW, MAKE THE BASELINE CORRECTION FOR THIS ABSORBANCE
C    BY DEFINING A BASELINE FROM ACTUAL SPECTRAL FEATURES.
C
C  DEFINE THE BASELINE POINTS FOR THE UPPER END OF THE
C  BAND (1141-1146 CM-1)
C
C    IPT3=1141/FXAX IPT4=1146/FXAX
C
C  AVERAGE THE POINTS FOR THE HIGHER CM-1 BASELINE LOCATION
C
C    SP = 0
C    BP1= 0
C    COUNT = 0
C    IFIRST=IPT3
C    ILAST =IPT4
C  PRINT*, ' '
C  PRINT*, '***** FIND THE CTFE 1130 CM-1 PEAK BASELINE PTS'
C  PRINT*, ' '
C
C  NOW CALCULATE FIRST BASELINE POINT
C
C    IF1=IFIRST*FXAX IF2=ILAST*FXAX
C
C    PRINT 46, IF1,IF2
C 46    FORMAT(' ','FIRST=',I4,2X,'LAST=',I4,/)
C    DO 71 I=IFIRST,ILAST
C      SP=SP+Y(I) COUNT=COUNT+1
C
C  CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C    WN=(I-1)*FXAX
C    PRINT 47,WN,Y(I),SP,COUNT
C 47    FORMAT(' ','WN=',F8.3,2X,'Y(I)=',F8.3,2X,'SP=',F8.3,
C    12X,'COUNT=',I6)
C 71    CONTINUE
C    BP1=SP/COUNT
C    PRINT*, 'BP1= ',BP1
C    PRINT*, ' '
C
C  DEFINE THE BASELINE POINTS FOR THE LOWER END OF

```



```

C THE BAND (1113-1117 CM-1)
C
C      IPT5=1111/FXAX IPT6=1117/FXAX
C
C
C AVERAGE THE POINTS FOR THE LOWER CM-1 BASELINE LOCATION
C
C      SP = 0
C      BP2= 0
C      COUNT = 0
C      IFIRST=IPT5
C      ILAST =IPT6
C
C NOW CALCULATE LOWER BASELINE POINT
C
C      IF2=IFIRST*FXAX IL2=ILAST*FXAX
C      PRINT 38, IF2,IL2
C 38  FORMAT(' ', 'FIRST=', I4, 2X, 'LAST=', I4, /)
C      DO 72 I=IFIRST, ILAST
C          SP=SP+Y(I) COUNT=COUNT+1
C
C CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C      WN=(I-1)*FXAX
C      PRINT 39, WN, Y(I), SP, COUNT
C 39  FORMAT(' ', 'WN=', F8.3, 2X, 'Y(I)=', F8.3,
C          &2X, 'SP=', F8.3,
C          12X, 'COUNT=', I6)
C 72  CONTINUE
C      BP2=SP/COUNT
C      PRINT*, 'BP2= ', BP2
C      PRINT*, ' '
C
C CALCULATE THE BASELINE CORRECTION. THERE ARE TWO POSSIBLE
C CASES: (A) POSITIVE SLOPING BASELINE, OR (B) NEGATIVE
C SLOPING BASELINE.
C
C CASE (A) - POSITIVE SLOPING BASELINE (BP1 < BP2)
C
C SKIP TO CASE (B) IF BASELINE SLOPE IS NEGATIVE
C IF(BP1.GT.BP2) GOTO 3010 C C OTHERWISE PROCEED WITH THE
C CORRECTION
C
C      PRINT*, ' '
C      PRINT*, '**** CASE (A) BASELINE CORRECTION ****'
C      PRINT*, ' (CTFE REFERENCE PEAK AT 1130 CM-1'
C      PRINT*, ' '
C      DP1=(1141+1146)/2 DP2=(1111+1117)/2 YDIF=BP2-BP1
C      XDIF=DP1-DP2 XDIF2=DP1-1131 FAC1=XDIF2/XDIF
C      FAC2=FAC1*YDIF FAC2=FAC2+BP1
C      PRINT 88, DP1, DP2, YDIF, XDIF, XDIF2, FAC1, FAC2
C 88  FORMAT(' ', 'DP1=', F8.3, 2X, 'DP2=', F8.3, 2X, 'YDIF=',
C          &F9.4, 2X, 'XDIF=', F9.4, 2X, 'XDIF2=', F9.4, 2X, /, 'FAC1=',
C          &F9.4, 2X, 'FAC2=', F9.4, /)

```

```

      GOTO 3510
C
C CASE (B) - NEGATIVE SLOPING BASELINE (BP1 > BP2)
C
3010 CONTINUE
C   PRINT*, ' '
C   PRINT*, '**** CASE (B) BASELINE CORRECTION ****'
C   PRINT*, ' (CTFE REFERENCE PEAK AT 1130 CM-1) '
C   PRINT*, ' '
      DP1=(1141+1146)/2 DP2=(1111+1117)/2 YDIF=BP1-BP2
      XDIF=DP1-DP2 XDIF2=1131-DP2 FAC1=XDIF2/XDIF
      FAC2=FAC1*YDIF FAC2=FAC2+BP2
C   PRINT 58, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 58   FORMAT(' ', 'DP1=',F8.3,2X,'DP2=',F8.3,2X,'YDIF=',
C   &F9.4,2X,'XDIF=',F9.4,2X,'XDIF2=',F9.4,
C   &2X,/, 'FAC1=',F9.4,2X,'FAC2=',F9.4,/)
3510 CONTINUE
C
C THE BASELINE-CORRECTED ABSORBANCE VALUE AT 1130.578 CM-1
C CAN NOW BE USED TO SUBTRACT OUT THE CTFE FROM THE
C OZONE SPECTRUM
C
C
C THE SCALE FACTOR IS DETERMINED BY THE RATIO OF THE
C BASELINE-CORRECTED CTFE ABSORBANCE VALUE AT 1130.578 CM-1
C IN THE REFERENCE SPECTRUM (MEASURED TO BE 0.270) AND
C THE BASELINE-CORRECTED CTFE ABSORBANCE VALUE AT COMPUTED
C MAXIMUM ABSORBANCE IN THE SAMPLE SPECTRUM
C
      AREF = PYA-FAC2
C   PRINT 89, AREF
C 89   FORMAT(35(' - '),/, ' ', 'PEAK ABS(1130 CM-1)= ',F6.3,/,
C   135(' - '),/)
C
      SCALE = ABS(AREF)/(0.270)
C   PRINT *, 'AREF= ',AREF,'SCALE=',SCALE
C
C SUBTRACT OUT THE CTFE CONTRIBUTION TO THE ABSORBANCE
C FROM 1037 TO 1074 CM-1 SO THAT OZONE ABSORBANCE CAN BE
C COMPUTED ACCURATELY
C   PRINT*, ' '
C   PRINT*, '*** SUBTRACT OUT ANY CTFE IN THE O3 BAND'
C   PRINT*, ' '
      IPT5 = 1037/FXAX
      IPT6 = 1074/FXAX
      DO 40 I= IPT5,IPT6
      J=I+1-IPT5
      TEM=Y(I)
      REF(J)=SCALE*REF(J)
      Y(I)=Y(I)-REF(J)
      L=I*FXAX
      M=J*FXAX
C   PRINT 42,L,TEM,Y(I),REF(J),M
C 42   FORMAT(' ', 'I=',I6,2X,'Y(I)=',F6.3,2X,'Y(I) CORR.=',

```

```

C      1F6.3,2X,'REF(J)=' ,F6.3,2X,'J=' ,I4)
40      CONTINUE
C
C      DEFINE THE BASELINE POINTS FOR THE HIGHER CM-1 OZONE
C      ANALYTICAL PEAK
C
C      PRINT*, ' '
C      PRINT*, '***** NOW, PRINT OUT THE BASELINE CORRECTION'
C      PRINT*, ' VALUES FOR THE O3 BAND'
C      PRINT*, ' '
C      IPT1=1070/FXAX IPT2=1074/FXAX
C
C      PRINT 45, IPT1,IPT2
C 45      FORMAT(' ', 'IPT1=', I4,2X, 'IPT2=', I4,/)
C
C      AVERAGE THE POINTS FOR THE HIGHER CM-1 BASELINE LOCATION
C
C      SP = 0
C      BP1= 0
C      COUNT = 0
C      IFIRST=IPT1
C      ILAST =IPT2
C
C      NOW CALCULATE FIRST BASELINE POINT
C
C      IF1=IFIRST*FXAX IL1=ILAST*FXAX
C      PRINT 36, IF1,IL1
C 36      FORMAT(' ', 'IFIRST=', I4,2X, 'ILAST=', I4,/)
C      DO 70 I=IFIRST,ILAST
C          SP=SP+Y(I) COUNT=COUNT+1
C
C      CALCULATE WAVENUMBER VALUES FOR PRINTOUT
C
C      WN=(I-1)*FXAX
C      PRINT 37,WN,Y(I),SP,COUNT
C 37      FORMAT(' ', 'WN=', F8.3,2X, 'Y(I)=' ,F8.3,2X,
C          &'SP=' ,F8.3,
C          12X, 'COUNT=' ,I6)
C      70      CONTINUE
C          BP1=SP/COUNT
C          PRINT*, 'BP1= ',BP1
C
C      THE LOWER CM-1 BASELINE POINT IS DEFINED AS THE VALLEY
C      MINIMUM
C      IN THE RANGE 1042-1045 CM-1 (OR IN DATA POINT VALUES:
C      2161-2167). THIS SECTION FINDS THE MINIMUM VALUE FOR THE
C      ABSORBANCE AND RECORDS THE CORRESPONDING CM-1 VALUE.
C
C      PRINT*, ' '
C      PRINT*, '***** FIND THE O3 PEAK MIN. IN THE RANGE OF'
C      PRINT*, ' 1042-1045 CM-1'
C      PRINT*, ' '
C      PXM= 0
C      PYM = 0

```

```

DO 75 K=2161,2167
  IF (Y(K).LT.Y(K-1)) THEN
    PYM=Y(K) IE=K-1 PXM=IE*FXAX
    PRINT 199,K,Y(K),PYM,PXM
    FORMAT(' ','K=',I4,2X,'Y=',F8.3,2X,
    &'PYM=',F8.3,2X,'PXM=',F8.3)
    ENDIF
  75 CONTINUE

    BP2=PYM
    PRINT*,'BP2= ',BP2

C
C DETERMINE THE X,Y VALUES (CM-1 AND ABS.) FOR THE OZONE
C ANALYTICAL PEAK (1055 CM-1) BY FINDING THE MAXIMUM Y VALUE
C IN THE INTERVAL FOR THIS PEAK WHICH IS: 1052 CM-1 TO 1058
C CM-1 (OR IN DATA POINT VALUES: 2182 TO 2194).
C
C
C PRINT*,' '
C PRINT*,'***** FIND THE O3 PEAK ABS. AT 1055 CM-1'
C PRINT*,' '
C
C PXA=0
C PYA=0
C MAX=0
C DO 82 I=2182,2194
C   IF (ABS(Y(I)).GT.MAX) THEN
C     MAX=Y(I) PYA=MAX
C     IC=I-1 PXA=IC*FXAX
C     PRINT 299,I,Y(I),PYA,PXA
C     FORMAT(' ','I=',I4,2X,'Y=',F8.3,2X,'PYA=',
C     &F8.3,2X,'PXA=',F8.3)
C     ENDIF
C   82 CONTINUE
C   PRINT 86,PXA,PYA
C 86 FORMAT(' ','PXA= ',F8.3,2X,'PYA= ',F8.3,/)
C
C CALCULATE THE BASELINE CORRECTION. THERE ARE TWO POSSIBLE
C CASES: (A) POSITIVE SLOPING BASELINE, OR (B) NEGATIVE
C SLOPING BASELINE.
C
C CASE (A) - POSITIVE SLOPING BASELINE (BP1 < BP2)
C
C SKIP TO CASE (B) IF BASELINE SLOPE IS NEGATIVE
C
C   IF(BP1.GT.BP2) GOTO 3000
C
C OTHERWISE PROCEED WITH THE CORRECTION
C
C PRINT*,' '
C PRINT*,'*** CASE (A) BASELINE CORRECTION FOR O3'
C PRINT*,' '
C DP1=(1070+1074)/2 DP2=(1042+1045)/2 YDIF=BP2-BP1
C XDIF=DP1-DP2 XDIF2=DP1-PXA FAC1=XDIF2/XDIF
C FAC2=FAC1*YDIF FAC2=FAC2+BP1

```

```

C      PRINT 87, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 87    FORMAT(' ', 'DP1=',F8.3,2X, 'DP2=',F8.3,2X, 'YDIF=',
C      &F9.4,2X, 'XDIF=',F9.4,2X, 'XDIF2=',F9.4,
C      &2X,/, 'FAC1=',F9.4,2X, 'FAC2=',F9.4,/)
C      GOTO 3500

C
C CASE (B) - NEGATIVE SLOPING BASELINE (BP1 > BP2)
C
C 3000  CONTINUE

C
C      PRINT*, ' '
C      PRINT*, '*** CASE (B) BASELINE CORRECTION FOR O3'
C      PRINT*, ' '
C      DP1=(1070+1074)/2 DP2=(1042+1045)/2 YDIF=BP1-BP2
C      XDIF=DP1-DP2 XDIF2=PYA-DP2 FAC1=XDIF2/XDIF
C      FAC2=FAC1*YDIF FAC2=FAC2+BP2
C      PRINT 57, DP1,DP2,YDIF,XDIF,XDIF2,FAC1,FAC2
C 57    FORMAT(' ', 'DP1=',F8.3,2X, 'DP2=',F8.3,2X, 'YDIF=',
C      &F9.4,2X, 'XDIF=',F9.4,2X, 'XDIF2=',F9.4,
C      &2X,/, 'FAC1=',F9.4,2X, 'FAC2=',F9.4,/)
C      3500 CONTINUE

C
C APPLY THE CORRECTION TO THE ABSORBANCE VALUE FROM PPK
C
C      CABS=PYA-FAC2

C
C PRINT OUT CORRECTED ABSORBANCE VALUE
C
C      PRINT 90, CABS
C 90    FORMAT(35(' - '),/, ' ', 'PEAK ABS(O3,1055 CM-1)= ',F6.3,/,
C 135(' - '),/)

C
C END THE SUBROUTINE
C
C      RETURN END

```

APPENDIX K

LISTING OF MS-EXCEL MACROS USED FOR DATA FORMATING (see APPENDIX A for a description of how the ASCII data file is acquired and sent to MS-EXCEL)

OPERATION: Once the appropriate ASCII data file is transferred to MS-EXCEL, the data is parced manually and the top 4 lines of the worksheet are left blank. Then the two macros listed here are run. Finally, the data columns are labeled according to the chemical species which are present in the experiments being conducted. The macros are stored under the file name NICOLET PROCESSING MACROS.

⌘-A

Record1
=SELECT("C1:C15")
=COPY()
=NEW(1)
=PASTE()
=SELECT("C1:C4")
=INSERT(1)
=SELECT("R1")
=INSERT(2)
=SELECT("C1:C12")
=ALIGNMENT(3)
=SELECT("C1")
=FORMAT.NUMBER("d-mmm-yy")
=SELECT("C2")
=FORMAT.NUMBER("0.0000")
=SELECT("C4")
=FORMAT.NUMBER("0.0000")
=SELECT("C5")
=FORMAT.NUMBER("GENERAL")
=SELECT("C9")
=FORMAT.NUMBER("0.0")
=SELECT("R2C4")
=FORMULA("=RC[2]+RC[3]/60+RC[4]/3600")
=SELECT("R2C3")
=FORMULA("=IF(R[1]C[1]>RC[1],IF(RC[1]>0.0001,1,0),0)")
=SELECT("R2C2")
=FORMULA("=24*SUM(R2C3:RC[1])+RC[2]-R2C4")
=SELECT("R2C1")
=FORMULA("=RC[4]+SUM(R2C3:RC[2])")

=SELECT("R2C1:R200C4")
=FILL.DOWN()
=SELECT("R1C1")
=RETURN()

Record2
=SELECT("C1:C2")
=COPY()
=HPAGE(4)
=HLINE(1)
=SELECT("C16:C17")
=PASTE.SPECIAL(3,1,FALSE,FALS E)
=HLINE(1)
=HPAGE(-4)
=SELECT("C4")
=COPY()
=HPAGE(4)
=SELECT("C18")
=PASTE.SPECIAL(3,1,FALSE,FALS E)
=HSCROLL(9,TRUE)
=SELECT("C9:C15")
=COPY()
=HPAGE(2)
=SELECT("C19:C25")
=PASTE()
=SELECT("C16:C25","R1C25")
=ALIGNMENT(3)
=SELECT("C16")
=FORMAT.NUMBER("d-mmm-yy")
=SELECT("C17:C18")
=FORMAT.NUMBER("0.0000")
=SELECT("C1:C15")
=EDIT.DELETE(1)
=SELECT("R1:R4")
=INSERT(2)
=SELECT("R4C1")
=FORMULA("DATE")
=SELECT("R4C2")
=FORMULA("ABS. TIME (HR)")
=SELECT("R4C3")
=FORMULA("TIME (HR)")
=SELECT("R4C4")
=FORMULA("TEMP (C)")
=SELECT("R4C5")
=FORMULA("SPECIES 1")
=SELECT("R4C6")

=FORMULA("SPECIES 2")
=SELECT("R4C7")
=FORMULA("SPECIES 3")
=SELECT("R4C8")
=FORMULA("SPECIES 4")
=SELECT("R4C9")
=SELECT.END(1)
=SELECT.END(1)
=COLUMN.WIDTH(10.571428571428,"C2")
=SELECT("R3C1")
=SELECT("R1C1:R2C1")
=ALIGNMENT(2)
=RETURN()